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RESEARCH AND INVESTIGATION OF
CATHODOLUMINESCENT PHOSPHOR FILMS
PREPARED BY SOLUTION SPRAYING

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FOREWORD

This report was prepared by the Research Division of The National Cash Register Company, Dayton, Ohio. This report summarizes the work performed during the period from 1 June 1962 through 31 August 1963 under Contract No. AF 33(657)-8985, BPSN: 2-6799-415605. This contract is administered by the Electronic Technology Division of the Air Force Avionics Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, with Mr. M. R. St. John serving as project engineer. Additional work is being performed under this contract.

The experimental studies described herein were made in the Physical Research Department, Mr. E. K. Prugh, Department Head. Project direction was provided by Dr. M. S. Hall. Other technical personnel assigned to this project were Mr. J. W. Gilliland, Jr., Mr. E. Reinmuller, and Mr. W. O. Evans. The following graduate students also contributed to this work during summer employment: Mr. J. Fortman and Mr. D. Smith. The x-ray diffraction studies were made by the Materials Analysis Department.

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ABSTRACT

The objective of this project was to determine the capabilities and necessary compromises in preparing cathodoluminescent films by a chemical solution spray process. This spray process is capable of forming cathodoluminescent films in situ on substrates which can withstand a spray temperature of 300° C and a heat treatment temperature of 600° C. Desired dopants may be incorporated by adding them to the spray solution. The cathodoluminescent film compositions investigated were: CdWO_4 , $\text{CdWO}_4:\text{Sm}$, $\text{CdWO}_4:\text{Ce}$, ZnWO_4 , $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{CdS}:\text{Ag}$, $\text{ZnS}:\text{Ag}$, and $\text{ZnCdS}:\text{Ag}$. Properties of these films were evaluated by x-ray diffraction analysis, by photo- and cathodoluminescent brightness and spectral emission, and by thermoluminescent "glow-curve" studies. In general, the luminescent properties of these sprayed films were found to be in agreement with the properties reported in the literature for phosphor powders of like compositions. Luminescent $\text{CdS}:\text{Ag}$ films were prepared with the (0002) plane of the crystallites preferentially oriented parallel to the substrate. No correlation between crystal orientation and cathodoluminescent efficiency was observed. Both ultraviolet irradiation and electron bombardment were used to excite the phosphor films for thermoluminescent studies. The glow curve for most samples increased in intensity for electron excitation and the shape of the glow curve for some samples changed with mode of excitation.

Publication of this technical report does not constitute Air Force approval of the findings or conclusions contained herein. It is published only for the exchange and stimulation of ideas.

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1.0 INTRODUCTION

This is a technical documentary report on the research and investigation of cathodoluminescent films prepared by solution spraying performed during the period June 1, 1962 through August 31, 1963. The objective of this project was to determine the capabilities and necessary compromises in forming cathodoluminescent films by the NCR solution spray process.

The solution spray process devised by NCR for forming films of inorganic compounds involves the spraying of a chemical solution onto a heated substrate. All elements needed in the desired film may be contained in the chemical solution with no component of the ambient atmosphere or substrate being required.

The capabilities of this spray technique in the preparation of cathodoluminescent phosphor films were explored by determining the physical properties of a variety of sprayed phosphor film compositions. In particular, cathodoluminescent films of CdWO_4 , $\text{CdWO}_4:\text{Sm}$, $\text{CdWO}_4:\text{Ce}$, ZnWO_4 , $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{CdS}:\text{Ag}$, $\text{ZnS}:\text{Ag}$, and $\text{ZnCdS}:\text{Ag}$ were prepared. Various physical properties of these films were investigated with emphasis on: (1) photo- and cathodoluminescent spectral emission, (2) electron trap distribution and density, (3) crystal structure, and (4) crystal orientation.

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2.0 PHOSPHOR SCREEN TECHNOLOGY

A brief review of the general phosphor screen requirements for sensory and display devices and of the state-of-the-art is included in the following paragraphs.

2.1 Sensory and Display Device Requirements

The function of cathodoluminescent screens in sensory and display devices is to convert the information present in an energetic electron beam or pattern into a luminescent output. This output may be used directly for viewing, used to excite a photosensitive material for further amplification, or used to excite a photosensitive recording medium. The performance of some sensory and display devices is limited by the characteristics of available phosphor screens.

The major device requirements for cathodoluminescent screens are: high cathodoluminescent efficiency, good resolution, a spectral emission appropriate for the specific application, and electron burn resistance.

The ideal phosphor screen would consist of a phosphor material having high intrinsic cathodoluminescent efficiency. There should be good optical and thermal contact between the phosphor and the substrate. The screen should have as much volume-scattering within the phosphor layer as is consistent with the resolution needed for a specific application. Too much light scattering degrades resolution but some volume-scattering is needed because in a clear transparent screen a large fraction of the luminescence is internally trapped and piped to the edge of the screen. The phosphor layer should have a minimum number of voids so that the energy of the impinging electrons may be efficiently utilized in as thin a layer as possible. In addition the phosphor material must be resistant

to change in efficiency with time due to electron bombardment.

2.2 Phosphor Screen Preparation Techniques

The phosphor screens commonly used today are prepared by forming a layer of phosphor particles. This is usually done by settling a dispersion of particles from a solution containing an appropriate binder such as potassium silicate. Although these powder screens have sufficient luminous efficiency for many applications, they have limited resolution and are somewhat susceptible to electron burn. Cataphoretic deposition is a process currently under development ⁽¹⁾ with the objective of producing improved phosphor powder screens.

Several of the ideal screen properties described above can be more easily obtained by using a phosphor film instead of a phosphor powder. The resolution and electron burn resistance properties of phosphor screens may be improved by using films. The reduced light scattering attainable with films leads to better image resolution. The higher density and good contact with the substrate obtained with films allows faster heat dissipation and improved electron burn resistance. Powder screens have found greatest usage to date because a phosphor powder can be selected which has high intrinsic cathodoluminescent efficiency, whereas film preparation processes must be developed which provide a means for forming films of phosphor materials having high intrinsic efficiency.

Two phosphor film preparation methods that have been under development for a number of years are: the vapor reaction method ⁽²⁾ and the evaporation method. ⁽³⁾

The vapor reaction method is chemically similar to a method frequently used for growing single crystals. ⁽⁴⁾ Vapors or gases containing

the elemental constituents of the desired solid are brought together and allowed to react to produce that solid. By appropriate control of such variables as the concentration of reactants, the vapor pressure of these, the freshness of the vapor mixture, etc., phosphor films can be grown on appropriately heated and nucleated substrates.

The vacuum evaporation of a commercial phosphor material onto a substrate has been tried by many experimenters. Some success has been achieved with this approach, ⁽⁵⁾ however, many difficulties are encountered. Selective and non-uniform evaporation of the phosphor dopants may cause loss of the luminescent centers. The host crystal may dissociate upon heating and lead to considerable departure from stoichiometry in the deposit. The deposit may be amorphous or have a different crystalline form from that of the original phosphor. The most successful evaporation method ⁽³⁾ is a two-step method in which a commercial phosphor material is first evaporated onto a glass substrate and the deposit is then fired in an appropriate atmosphere to reconstruct the crystalline phosphor. In some cases the condensed deposit is reacted with the substrate itself to obtain the desired phosphor composition.

In most cases the vapor reaction and vacuum evaporation methods have been studied with the objective of preparing transparent phosphor films. Kirk and Schulman ⁽⁶⁾ have described another method for preparing transparent luminescent films of zinc and cadmium silicate phosphors. Suitable solutions of zinc chloride or cadmium iodide with activator are sprayed onto Pyrex or silica glass preheated to 850° to 1,000° C. Direct reaction with the glass yields cathodoluminescent silicate films.

3.0 OUR APPROACH TO THE PROBLEM

Phosphor screens with improved properties are needed for sensory and display devices. Phosphors prepared in film form may provide improved phosphor screens if a suitable process can be found for preparing phosphor materials in situ on a substrate such that these materials have good cathodoluminescent efficiency.

The National Cash Register Company has developed proprietary solution spray processes for the preparation of films of inorganic compounds including many phosphor compositions. The subject of this study is the properties of cathodoluminescent films prepared by these solution spray processes.

The NCR solution spray process does not require the complex apparatus and preparation procedures (vacuum system or special atmosphere, such as H_2S) needed for the vapor reaction and evaporation methods. The NCR solution spray process also differs from that of Kirk and Schulman⁽⁶⁾ in several significant ways. The most important difference is that all elements needed in the desired film may be contained in the chemical solution with no reaction with the substrate being required.

The following general approach is used in the experimental investigation of the luminescent properties of sprayed phosphor films. First, a spray solution is designed to yield films having a chemical composition similar to that of a material known to yield efficient cathodoluminescence in powder form. A sufficient quantity of this solution is sprayed onto soft-glass microscope slides, held at about 300° C, to form a film a few microns thick. The film samples on microscope slides are then placed in a tube furnace and heated in flowing nitrogen for from 15 minutes to one hour at 600° C. The heat treated samples are examined for

photoluminescence under an ultraviolet lamp and for cathodoluminescence in a small evacuated bell jar with Tesla coil excitation. If promising luminescence is obtained, a second major experimental phase is undertaken to improve the luminescent properties. The improvement procedures include appropriate changes in spray solution compositions, spray rate, substrate temperature during spray, substrate material, heat treatment procedure, heat treatment time, and heat treatment atmosphere.

The first step in the general experimental approach outlined above was completed before this contract began. Spray solutions had been designed and a number of phosphor compositions had been prepared by spraying. The more promising compositions were: zinc sulfide;manganese -- ZnS:Mn , cadmium sulfide:silver -- CdS:Ag , zinc silicate;manganese -- $\text{Zn}_2\text{SiO}_4\text{:Mn}$, calcium tungstate -- CaWO_4 , magnesium tungstate -- MgWO_4 , cadmium tungstate -- CdWO_4 , zinc germanate;manganese -- $\text{Zn}_2\text{GeO}_4\text{:Mn}$, cadmium borate;manganese -- $\text{Cd}_2\text{B}_2\text{O}_7\text{:Mn}$, zinc borate;manganese -- $\text{Zn}_2\text{B}_4\text{O}_9\text{:Mn}$, and zinc phosphate;manganese -- $\text{Zn}_3(\text{PO}_4)_2\text{:Mn}$.

With this extensive list of promising film compositions at hand together with obvious possible variations, the selection of a composition with which to begin extensive experimental investigation was quite arbitrary. Cadmium tungstate was selected as the composition with which to begin.

During the period covered by this report various physical properties of the following phosphor film compositions were explored: (1) cadmium tungstate -- CdWO_4 , zinc tungstate -- ZnWO_4 , cadmium tungstate doped with samarium -- $\text{CdWO}_4\text{:Sm}$, and cadmium tungstate doped with cerium --

$\text{CdWO}_4:\text{Ce}$, (2) three luminescent phases of zinc silicate; manganese --
 $\text{Zn}_2\text{SiO}_4:\text{Mn}$, and (3) cadmium and zinc sulfide doped with silver --
 $\text{CdS}:\text{Ag}$, $\text{ZnS}:\text{Ag}$ and $\text{ZnCdS}:\text{Ag}$.

The experimental procedures and apparatus used for sample preparation and sample evaluation are described in the following section.

4.0 EXPERIMENTAL PROCEDURES AND APPARATUS

4.1 Phosphor Film Sample Preparation

The first steps in the preparation of a phosphor film by solution spraying is the preparation of a stable chemical solution which contains all of the elemental components of the desired phosphor. The elemental components must be present in the solution in the appropriate ratios and the chemicals used to provide these elements should have high purity in order to obtain good luminescent properties.

4.1.1 Solution Spraying

The basic arrangements used for the application of sprayed films is to maintain the substrate at an appropriate temperature with a hot plate and apply the solution to these heated substrates in a fine spray. The temperature of the substrates must be sufficient to evaporate the solvent, induce a reaction of the desired film components, and volatilize various unwanted components contained in the original solution.

The substrate temperatures used range from 250 to 450° C, depending upon the composition being prepared. Corningware electric skillets are convenient, commercially available hot plates for this purpose. Another effective hot plate was made from a cast iron plate by inserting immersion heaters in wells parallel to the surface of the plate.

The spray nozzle may be mounted stationary or moved by a suitable transport mechanism. Many exploratory sprays were made with a mounted or hand-held chromatographic spray bottle. The film properties are somewhat dependent upon the location of the sample in a fixed spray pattern. Improved film uniformity may be obtained by using a motor driven oscillating spray nozzle.

The important interdependent spray parameters are: substrate temperature, solution concentration, and rate of spray or solution flow rate. These will be discussed in more detail in Section 5 in connection with some of the phosphor film compositions that were prepared.

4.1.2 Heat Treatment

Heat treatment of the sprayed film improves the luminescent efficiency of most samples. Various temperatures, times, and atmospheres may be used to find those conditions which give the best results. The maximum temperature used is limited by the substrate. These limits are: 650° C for soft glass, 750° C for Pyrex, and 1,200° C for quartz. The heat treatment atmospheres explored were air, oxygen, nitrogen, and hydrogen sulfide. Air is the atmosphere usually used in heat treating the oxygen-dominated phosphor samples and nitrogen is normally used when heat treating sulfur-dominated phosphor samples.

A Hevi-Duty T-70 combustion tube furnace is suitable for heat treatment. This furnace is a two element, side opening, split-shell furnace capable of operation up to 1,000° C. The heat treatment atmosphere is controlled by connecting the desired gas supply to one end of the combustion tube and a bubble-tower trap to the exit end of the tube.

Covering the films during heat treatment usually improves the luminescent properties. Several different covering techniques are used. The simplest is merely placing a clean substrate over the film sample so that the film is sandwiched between the substrate on which it has been sprayed and another clean substrate. A second technique is to cover the sample in the above manner and then embed this sandwich

in a phosphor powder having the composition of the film being prepared. In some cases the film sample may be covered directly with the powder, but it is then usually difficult to remove all of the powder from the heat treated film.

4.1.3 Substrates

The substrate material must withstand the spray and heat treatment temperatures required with this process. Glass or ceramic substrates are the most appropriate substrate materials. Soft glass (commercial microscope slides), Pyrex, and quartz were used for most of this work. The substrates must be carefully cleaned for best results. The following substrate cleaning procedure was used: (1) toluene spray rinse - polyethylene bottle, (2) denatured alcohol spray rinse - polyethylene bottle, (3) hot chromic acid rinse - one minute at 60° C, (4) distilled water rinse - substrates may be stored in distilled water at this point, (5) acetone spray rinse - polyethylene bottle, and (6) air dry.

The possibility of preparing sprayed phosphor films on metal substrates was explored. Copper, aluminum, and stainless steel were used. Copper oxidized badly at the hot plate temperatures (300-425° C) used while spraying. Aluminum melts (660° C) below the heat treatment temperature needed for good luminescence with some phosphor film compositions. Luminescent films were successfully prepared on stainless steel; however, the film adherence was poor.

Bright green luminescent $\text{Zn}_2\text{SiO}_4\text{:Mn}$ sprayed films were obtained on stainless steel by heat treating in nitrogen for one hour at 1,150° C. However, the film adherence was very poor and the stainless steel surface was discolored.

Cadmium tungstate films do not require as high a heat treatment temperature as do the zinc silicate films. CdWO_4 films when sprayed onto aluminum or onto stainless steel and fired at 500°C showed fair blue cathodoluminescence. Adherence was also a problem with these films, but it was not as bad as with the zinc silicate samples. Several attempts were made to spray thick CdWO_4 films. The thickest film obtained on stainless steel and having fair adherence was about 10 microns thick.

The probable major cause for poor adherence of sprayed films on metal substrates is the difference between the thermal expansion of the film and that of the substrate. Better adherence could probably be obtained if a metal were used which provides a better match of thermal expansion and also withstands the required processing temperatures without chemical interaction with the sprayed film. Adherence has not been a serious problem when phosphor films are sprayed on glass or ceramic substrates.

4.2 Sample Evaluation

After the phosphor films have been sprayed and heat treated they are ready for evaluation of their physical properties. The physical measurements emphasized during this study were: (1) the crystallinity and crystal orientation as determined by x-ray analysis, (2) the photo- and cathodoluminescent brightness and the cathodoluminescent efficiency, (3) the spectral distribution of the photo- and cathodoluminescence, and (4) the electron trap density and distributions as determined from thermoluminescent "glow curves". The apparatus and experimental procedures used for these measurements are discussed below.

4.2.1 X-ray Analysis

X-ray diffraction and x-ray fluorescence were used to examine the sprayed phosphor films. X-ray diffraction was used to determine the crystal structure, the crystallite size, and the crystal orientation within the film. X-ray fluorescence was used where appropriate to determine the ratios of elements contained in the phosphor film samples compared with the ratios used in the spray solution.

A question of particular interest in this study was whether luminescent films could be prepared which had a preferred crystal orientation, and if so, whether such a preferred orientation would affect the cathodoluminescent efficiency. That a preferred crystal orientation might be found in certain sprayed phosphor films was suggested by results obtained in previous NCR studies ⁽⁷⁾ of CdS and CdSe films. The method illustrated by the following example was used to study crystal orientation. Figure 1 shows a sketch of x-ray diffraction data for a sprayed CdSe film. In a diffraction pattern for randomly oriented CdSe crystals the (100) peak would be the most intense; the horizontal dashes in Figure 1 show the expected height for the various peaks relative to the (100) peak for a randomly oriented sample. By the deviation of the diffraction pattern in Figure 1 from the pattern expected for random crystal orientation, it can be seen that the crystals are preferentially oriented with the (110) plane parallel to the substrate. The results obtained with luminescent CdS films are discussed in Section 5.5.

4.2.2 Luminescent Brightness and Efficiency

The luminescent properties of the sprayed and heat treated films are first evaluated qualitatively. The photoluminescent brightness, color and uniformity are observed with 2537 Å or 3650 Å

ultraviolet excitation. A similar qualitative evaluation of the cathodoluminescent properties is made by placing the film samples in a small bell jar and using a Tesla coil for excitation after the bell jar has been evacuated to about 10^{-2} mm Hg with a mechanical pump. These qualitative evaluations are used to give direction to the sample preparation procedures in the early stages of working with a particular phosphor composition.

Quantitative measurements of the cathodoluminescent properties of selected phosphor film samples are made with a demountable electron beam system. Two demountable systems are now available for such measurements. The system shown in Figure 2 was constructed using a 4" x 6" Pyrex pipe cross with appropriate fittings. An electrostatic deflection electron gun is mounted at one end. This gun supplies beam currents up to 20 microamperes and can be operated at beam voltages up to 50 kv by using post-deflection acceleration. The Pyrex cross is mounted on an oil diffusion pumping system using Silicon DC-704 oil, Viton gaskets, and trapped with liquid nitrogen. A vacuum of 10^{-6} mm Hg is readily attained with this system.

A second demountable electron beam system was completed near the end of this period. This system, shown in Figures 3 and 4, is pumped by a 200 liter/second Ultek getter-ion pump. This system eliminates possible contamination by oil backstreaming and is also free of vibration. Most of our future cathodoluminescent measurements will be made with this system.

The sprayed phosphor film samples are metallized before efficiency measurements are made. Vacuum evaporated aluminum films are used to metallize the phosphor samples. The reflectivity of

the aluminum film enhances the screen efficiency and the conductivity of the aluminum film prevents charge build up on the phosphor.

The cathodoluminescent efficiency of a sample may be determined by measuring the luminance with a Spectra Spot Brightness Meter while the sample is excited with a known beam current density and beam voltage. The electron beam is deflected into a carbon Faraday cage and the beam current is adjusted to the desired value (usually one microampere). The slightly defocused beam is then deflected to form a rectangular raster on the sample being tested. From the beam current, the raster area, the beam voltage, and the luminance the cathodoluminescent efficiency may be calculated by using the following formula:

$$\text{Efficiency in lumens/watt} = \frac{\left(\frac{\text{Luminance in foot-lamberts}}{\text{Beam Potential in volts}} \right) \left(\frac{1.076 \times 10^{-3} \text{ lumens}}{\text{cm}^2 \text{ foot-lamberts}} \right)}{\left(\frac{\text{Beam Current Density}}{\text{in amperes/cm}^2} \right)}$$

4.2.3 Spectral Emission

The apparatus used for measuring the spectral emission characteristics of the sprayed phosphor films is shown schematically in Figure 5, and by photographs in Figure 6 and 7.

A Perkin-Elmer Model 99 double-pass monochromator was equipped with a 6217 photomultiplier (S-10 response). This photomultiplier was calibrated against a thermocouple detector to determine its constant incident energy response. Since the Perkin-Elmer monochromator uses a prism for dispersion, the slit width on the monochromator was adjusted for each wavelength setting to give a constant spectral slit width, i.e. a constant wavelength interval falling on the exit slit.

Photoluminescence measurements were made with the apparatus shown in Figure 7. The sample was mounted in front of the entrance slit of the Perkin-Elmer monochromator. Monochromatic ultraviolet excitation was supplied by passing the emission of a Hanovia mercury lamp through a Bausch and Lomb grating monochromator. Secondary reflections were excluded by using a Corning 7-54 filter. Cathodoluminescence was obtained by mounting the samples inside a demountable cathode-ray tube as shown in Figures 4 to 6 and bombarding with electrons of 15 kv and about $1 \mu\text{A}/\text{cm}^2$ current density.

An NJE Corporation Model S-325 high voltage supply was used to supply 750 volts to the photomultiplier. Signal amplification was accomplished by means of a Tektronix preamplifier Type 53/54B and a Perkin-Elmer Model 107 amplifier. The intensity of light was recorded for one-half minute at each wavelength setting with a Varian Recorder Model G-11A.

A program to correct spectral curves was written for the NCR 102D computer during the performance of Contract AF 33(616)-3837 in 1958 (WADC TR 58-645). This program was resurrected and used: (1) to correct the luminescent spectra for the constant incident energy response of the photomultiplier, (2) to normalize the corrected data, and (3) to plot the normalized corrected data.

The program is suitable for all spectra lying within the limits of 400 to 700 m μ . Other spectra were corrected and plotted without the aid of the computer.

4.2.4 Thermoluminescence

The purpose of the thermoluminescence or glow curve studies was to further clarify the physical nature of the phosphor films and

to determine the effects of various processing parameters on the film properties. Some theoretical considerations are discussed briefly below followed by a discussion of our experimental arrangement and procedure. The glow curve results for representative samples of various phosphor film compositions are presented under Section 5.0.

When a crystalline material is irradiated with UV light below the absorption edge or bombarded with energetic cathode rays, electrons will be excited into the conduction band. In this state an electron moves with relative freedom through the crystal until it finds a position of lower potential energy which it may assume by one of two processes - recombination or trapping. In the first case an electron recombines with a positive hole at a luminescent center or in the valence band and returns to the ground state. Most recombination transitions result in the emission of a photon for efficient luminescent materials. However, some recombinations are radiationless transitions which heat the crystal lattice instead of contributing to the luminescence.

In the case of trapping, the electron assumes a metastable position with potential energy between the conduction band and the ground state. Trapping may occur in several ways. The electron may become trapped at a lattice imperfection such as a negative ion vacancy, or it may become attached to an impurity in the crystal. Also, if the temperature of the crystal is sufficiently low, the electron may polarize the surrounding material and become self-trapped. ⁽⁸⁾ Thus several different types of traps may exist in a crystal and there is for each type of trap a characteristic energy of activation for release of the electron. A simplified model of the electron trap is shown in Figure 9. In order to be excited from the filled or valence band into the conduction

band, an electron must be supplied at least energy E_c . From the conduction band, an electron may then undergo a recombination transition, or fall into a trap.

In order to be released from a trap of depth E , an electron must absorb at least an amount of energy E . Thus, when a substance is excited at low temperatures and then warmed at a constant rate, intensity maxima will be observed in the glow at different temperatures corresponding to the various trap depths which are present in the crystal. The probability p of an electron escaping from a trap of depth E at temperature T is given by the Boltzmann factor,

$$p = se^{-E/kT}$$

where k is Boltzmann's constant and s is an escape factor which is assumed to be constant although it may vary slightly with temperature. Randall and Wilkins ⁽⁹⁾ have calculated the form of the glow curve when E is single valued and the temperature rises at a constant rate. They assume there is no retrapping but that when an electron is released from a trap it goes directly to a luminescence center. Under these conditions their theoretical curve rises exponentially at first reaching a maximum and then falling to zero. The temperature at which maximum glow occurs varies slightly with rate of warming. From their theoretical calculations, Randall and Wilkins give the following approximation for converting the temperature of maximum glow to trap depth:

$$\text{Trap depth} = 25 kT_g$$

where k is Boltzmann's constant and T_g is the temperature of maximum glow in degrees Kelvin.

Garlick ⁽¹⁰⁾ has extended the development of Randall and Wilkins to include retrapping for the case when the capture cross section is the same for a trap as for an empty luminescence center. This treatment results in a fundamental change in the form of the decay at constant temperature from exponential to hyperbolic. There is also considerable modification of the glow curve. For example, the half-intensity width is larger by a factor of about two than for the case when retrapping was neglected. In either case, the temperature of maximum emission is proportional to the trap depth, the half-intensity width increases with temperature, and the peak intensity decreases with increasing temperature if the number of electrons trapped remains constant. For the complex trap distributions generally found in phosphors, the theoretical treatment becomes complex, and it is difficult to determine whether retrapping is important or not, but Garlick cites experimental evidence which shows that the neglect of retrapping is justified to a considerable extent.

A picture of glow curve apparatus used in our studies is shown in Figure 8. A schematic diagram of this glow curve apparatus is shown in Figure 10. The sample is mounted on the flat portion of the sample holder by clamps. A copper-constantan thermocouple (reference junction at 0° C) is pressed against the film by one of the clamps. A clump of solder with one side flat surrounds the junction to give more contact area between the thermocouple and sample. The signal from the thermocouple is fed into a Varian strip chart recorder, Model G-11A, to be recorded as a function of time and to the x-input on a Moseley X-Y recorder Model 2A "Autograf". The y-input on the X-Y recorder is from a 1P21 photomultiplier tube, powered by a Photovolt Photometer (Model

520M) power supply and amplified by a Keithley Model 410 micromicro-ammeter. Thus the glow curve (thermoluminescence intensity vs temperature) is recorded directly.

In the first part of this work a 70 watt heater was used which consisted of a lavite frame wound with a nichrome heating element, the whole assembly being contained inside the sample holder of anodized aluminum. This heater was subsequently replaced with a 50 watt Chromalox sealed cartridge heating element inside a brass sample holder. The latter heater overcame a serious disadvantage of the former -- a visible glow at high temperature which interfered with the glow curve in that range.

The heating rate during warm-up was controlled by the manual setting of a variac and by an automatic heating rate regulator. The variac, which was set prior to beginning a warm-up, controlled the upper limit of voltage which could be applied to the heater. The programmed heating rate regulator was used to maintain a constant heating rate over a wide temperature range. This device consisted of a variac whose setting was determined by the position of two closely spaced wires on a strip chart. The two wires were driven so as to follow the edge of a conducting strip painted on the chart paper. Thus, a program could be painted on the chart for any desired heating rate, which then could be reproduced at will.

Heating rates used for the glow curve measurements ranged from 12° C to about 40° C per minute. The heating rate was nearly constant in a single run (variations were no greater than 2 or 3° C per minute). The exact position of the glow maximum is somewhat dependent on the heating rate. But a few degrees difference makes only a small

difference in the energy level of the trap. It may be seen from Randall and Wilkins' conversion equation (trap depth = $25 kT_g$) that an error of $50^\circ K$ in the temperature of maximum glow would cause an error of only 0.1 ev in trap depth. Thus, any error resulting from a difference in heating rate would certainly be less than 10%.

Small variations in the intensity of the glow can be attributed to differences in the size of the sample, in the geometry, or in excitation intensity. These parameters, however, would not cause an intensity variation of more than a factor of two. Thus, any larger intensity changes between two samples may be considered significant in terms of the basic mechanism.

The sample holder assembly fitted inside a quartz tube which was evacuated to prevent formation of ice inside the tube when cooled in liquid nitrogen. The Dewar flask also was specially constructed of quartz (initially a Pyrex Dewar was used) to pass 2537 \AA UV light which was necessary for excitation of some of the samples.

In order to obtain cathodoexcitation for thermoluminescence a high frequency arc discharge produced by a Cenco Tesla coil was used. An insulated wire was fed through the brass top of the sample holder tube with an exposed end just in front of the sample but not touching it. The outside end of the wire was placed in contact with the tip of the Tesla coil. When the tube was evacuated, an arc could be obtained between the wire and the sample, thus exciting the sample and producing luminescence. For photoexcitation, the sample was irradiated with 2537 \AA or 3650 \AA UV light from a Bausch and Lomb Monochromator using a Hanovia Hg-lamp.

External light was excluded from the photomultiplier

tube by wrapping the Dewar with black tape, covering the openings around the top of the flask with black cloth, and using a black rubber fitting between the photomultiplier casing and the window casing on the Dewar. No room light could be detected by this arrangement although very low levels of thermoluminescence could be detected. The lower limit of detectability of the tube was set by the dark current which was about 3×10^{-11} amperes.

The quartz tube containing the sample was evacuated and immersed in liquid nitrogen contained in the Dewar. A low temperature of between -180°C and -190°C was attainable in this manner. The sample was then excited either by UV irradiation or by Tesla coil bombardment for about three minutes. This time was sufficient for the traps to be filled to equilibrium. During the excitation and subsequent warm-up, ambient light was excluded from the sample and from the photomultiplier tube.

There was about a one minute time lapse between excitation and the beginning of the warm-up. This was to allow the photomultiplier power supply a warm-up time and also for the decay of short term phosphorescence. The glow curve was then recorded on the X-Y recorder and the heating rate recorded on the Varian strip chart recorder.

Some other studies of trap distribution were made using "decayed" glow curves. This term refers to the glow curve obtained from a sample in which some of the traps have been emptied by warming, and then recooling. If a single trapping level is involved, no change other than in intensity would occur in the form of the glow curve. However, if multiple trapping states are present, the "decayed" glow curve would peak at higher temperatures, since the shallower traps would have been emptied first in the initial warm-up.

5.0 RESULTS AND DISCUSSION

The experimental results for this period are presented and discussed in this section. The results are grouped according to film composition (tungstates, silicates, and sulfides) in the first three subsections. The fourth subsection deals with the general factors affecting the efficiency and resolution of a phosphor screen. The final subsection presents the results of a preferred crystal orientation study in luminescent CdS films.

5.1 Tungstates

Photoluminescent emission spectra are shown in Figure 11 for ZnWO_4 , CdWO_4 , and $\text{CdWO}_4:\text{Sm}$ for 254 millimicron exciting light. The emission spectra of ZnWO_4 and CdWO_4 are seen to be almost identical, both maxima occurring at 470 $\text{m}\mu$. The addition of samarium as a dopant in CdWO_4 has no apparent effect on this main band of luminescence but produces three smaller bands at 565 $\text{m}\mu$, 610 $\text{m}\mu$, and 660 $\text{m}\mu$. The blending of these new peaks with the original blue results in a whiter color. The atomic ratio of Cd to Sm is about 88 to 1 in the sample whose spectrum is given. These three samarium peaks are similar to those observed at -196°C by Keller and Pettit ⁽¹¹⁾ in BaTiO_3 doped with samarium.

The luminescence efficiency of the tungstates was observed to be a function of temperature. Cathodoluminescence of the samples was observed visually at temperatures between -200°C and $+200^\circ\text{C}$ with samples mounted in the glow curve apparatus in order to obtain the various temperatures. CdWO_4 , ZnWO_4 , and $\text{CdWO}_4:\text{Ce}$ have their characteristic blue color and about a constant brightness between -180°C and $+25^\circ\text{C}$. At higher temperatures the brightness decreases and at about $+200^\circ\text{C}$ the luminescence is almost completely quenched. No color change was apparent in these films over the temperature range explored. The

cathodoluminescence of $\text{CdWO}_4:\text{Sm}$ is blue-green at -170°C ; at room temperature it is bluish white with a tinge of pink; and at $+200^\circ\text{C}$ the color is red-orange. Kroger ⁽¹²⁾ shows a graph of the quantum efficiencies versus temperature for the blue CaWO_4 band and the red samarium band in $\text{CaWO}_4:\text{Sm}$. It is shown that the blue band decreases to very small efficiency at 150°C and above, whereas the red band increases to its maximum at about 200°C and above. At temperatures below 0°C the situation is reversed and 90% of the change occurs between 0 and 100°C . Our observations on $\text{CdWO}_4:\text{Sm}$ are in close qualitative agreement with those given by Kroger for calcium tungstate doped with samarium.

The glow curve of CdWO_4 (Figure 12) shows a surprising amount of structure considering that there is no doping. Note the dependence of intensity on the mode of excitation. In every phosphor studied so far, with the exception of the green luminescent phase of $\text{Zn}_2\text{SiO}_4:\text{Mn}$, excitation by electron bombardment (with Tesla coil) has resulted in more intense thermoluminescence than with ultraviolet excitation.

This dependence upon mode of excitation is presumably due to the ultraviolet rays' being strongly absorbed at the surface of the film, thus exciting only that part of the film close to the surface, whereas the electrons are energetic enough to penetrate into the film and excite a greater volume. If all traps are evenly distributed throughout the bulk of the film, then the only difference between electron and UV excitation should be in intensity. However, suppose a particular trap is concentrated near the surface of the film, or is associated with a surface imperfection in the crystal structure. Such a trap would have a greater effect on the glow curve, relative to the other traps, when ultraviolet

radiation was the source of exciting energy.

Such an effect appears to be present in the glow curves of both CdWO_4 (Figure 12) and $\text{CdWO}_4:\text{Sm}$ (Figure 13). The CdWO_4 glow curve excited by UV has a peak at about -70°C . But when electron bombardment excitation is used, all the other peaks become about ten times larger while the -70°C peak apparently is no more intense and so is masked.

In Figure 13 the glow curve of $\text{CdWO}_4:\text{Sm}$ apparently consists of two primary peaks, very close together, whose heights relative to each other depend on the mode of excitation. In this case those traps associated with a surface phenomenon are the deeper ones (-104°C peak), whereas the shallower traps (-127°C peak) are distributed more evenly throughout the bulk; or it might be that the glow curve of $\text{CdWO}_4:\text{Sm}$ results from a single trapping level provided by the samarium ion, with the original traps of the undoped lattice adding on to these.

In $\text{CdWO}_4:\text{Ce}$ ultraviolet excitation yielded thermoluminescence barely above detectable limits, while electron excitation yielded a glow curve with more intensity as shown in Figure 14. There is some similarity between the glow curves of CdWO_4 and $\text{CdWO}_4:\text{Ce}$ although the peaks do not exactly correspond. The physical nature of the traps might be very similar in the two cases with the actual trap depths being affected by the addition of cerium in the one case. Cerium as a dopant, however, does not appear to contribute directly to the formation of trapping states since the intensity of the glow in $\text{CdWO}_4:\text{Ce}$ is of the same order of magnitude as that of the undoped CdWO_4 . In ZnWO_4 a surface effect, if present at all, was not clearly shown, but the intensity was different by a factor of about 40 between the two excitation modes. Only the more intense glow curve

excited by electron bombardment is shown in Figure 15.

These traps which are associated with the surface might be crystal imperfections which are more prevalent near the surface. Even the discontinuity of the crystal itself at the surface could constitute the imperfection. Other possibilities are that changes in stoichiometry may occur near the surface or that some impurity may be absorbed at the surface.

The trap depths corresponding to the various glow peaks in the tungstate and silicate films are given in Table 1.

5.2 Silicates

Three luminescent phases were observed in sprayed $\text{Zn}_2\text{SiO}_4\text{:Mn}$ films. Red, yellow, and green cathodoluminescent colors were obtained using the same " $\text{Zn}_2\text{SiO}_4\text{:Mn}$ " spray solution. The color depended upon the substrate material and heat treatment used. Films on Pyrex, quartz, or stainless steel and heat treated at 650°C for one hour in air showed orange to red cathodoluminescence. Green was obtained when films on stainless steel or quartz were heat treated at $1,150^\circ\text{C}$ for one hour in nitrogen. Films on commercial microscope slides heat treated at 650°C in air and films on Pyrex heat treated at 750°C in air showed yellow or yellow-green cathodoluminescence. Feldman and O'Hara ⁽¹³⁾ observed similar luminescent phases in their studies of evaporated Willemite films.

Glow curve studies were conducted on $\text{Zn}_2\text{SiO}_4\text{:Mn}$ in all three of its luminescent forms -- red, yellow, and green. Exciting energy was obtained from $2,537 \text{ \AA}$ UV light and by electron bombardment (Tesla coil). The latter form of excitation was used on all three forms. The red and yellow forms are not excited by UV so that UV-excited glow curves were only obtained from the green form.

In Figure 16 are glow curves typical of the green and yellow emitting forms of $\text{Zn}_2\text{SiO}_4:\text{Mn}$. The thermoluminescence in the green form is independent of the mode of excitation. Between -180°C and 25°C a considerable variation occurs in the glow curves from one form to the next. The red form is similar to the yellow form, but has still less structure in the curve than the yellow form. A high temperature peak is present on all three forms in the range of $150\text{-}200^\circ\text{C}$.

These results can be correlated with the idea that crystallinity decreases from the green phase to the yellow to the red, ⁽¹⁴⁾ if it is assumed that the electron traps which contribute to the glow peaks between -180°C and 25°C are associated with the crystal structure and the trap contributing to the high temperature peak is associated with the manganese ion. Thus the decreased crystallinity in the yellow and red forms would account for their lower intensity glow curve having less distinct structure between -180°C and 25°C while the high temperature glow peak would be similar in all of the forms since they all contain manganese in equal amounts. The glow curve of commercial powdered $\text{Zn}_2\text{SiO}_4:\text{Mn}$ (green) corresponds fairly closely to those of the sprayed films except that the 150°C peak is much smaller in the powder. This would, in terms of the mechanism discussed above, simply indicate a smaller concentration of manganese in the powder.

$\text{Zn}_2\text{SiO}_4:\text{Mn}$ films of the green emitting form have a bright, pure green luminescence. The luminescent emission spectrum peaks at $520\text{ m}\mu$ as shown in Figure 17 and has the narrowest emission band of all the phosphor films studied.

5.3 Sulfides

Emission spectra are shown in Figure 18 for films of $\text{CdS}:\text{Ag}$,

ZnCdS:Ag, and ZnS:Ag. These spectra are in general agreement with those reported in the literature by a number of investigators. But the spectrum of each of these can always be shifted somewhat by varying the processing parameters so that small differences between experimenters are to be expected.

In Figure 19 it is seen that the wavelength of the spectral emission peak as a function of the mole percent of ZnS in the film is very close to linear. The points given by Drozd and Levshin ⁽¹⁵⁾ appear to show a slight nonlinearity whereas our data do not. However, they were working with self-activated systems and the shorter wavelength emission in our samples throughout the range is presumably due to silver activation. In either case the function is very close to linear. Our experimental points do not deviate far from the line, indicating composition changes during processing and other experimental errors are not large.

During heat treatment at 650°C, even under a flowing nitrogen atmosphere, oxidation occurred in samples of 90-100 mole percent ZnS, causing a nonuniform luminescence color over the sample. This oxidation effect produced a shift in the spectral emission from a deep blue, characteristic of high ZnS content compositions, to the green-blue characteristic of ZnO. This change was especially strong around the edges of the film. Drozd and Levshin reported heat treatment of their powder samples at 900°C in a closed quartz crucible in air. This leads one to suspect that the departure from linearity in their data at high ZnS content might have been the result of oxidation effects and the true function of peak emission versus ZnS content is a linear one. In fact, such a departure from linearity was apparent in our own data before the embedded covering technique was used for heat treating ZnS films.

Glow curve studies were made on ZnCdS_xAg films with various ratios of zinc to cadmium. The glow curve peak is strongly dependent upon the ratio of ZnS to CdS in the film, as is shown in Figure 20. The relation appears to be quite close to linear, although a limited range of compositions was covered.

Hoogenstraaten ⁽¹⁶⁾ has shown that such linear or near linear relationships between glow peak temperature and ZnS concentration exist in ZnCdS phosphors with a wide variety of activators and coactivators. The glow peak temperatures in his studies ranged from liquid nitrogen temperature up to almost 400° C.

Since the lowest attainable temperature with liquid nitrogen as the coolant is about -185° C, it was not possible to study compositions below about 75% ZnS because of their lower temperature peaks. If the glow peak occurs too close to the starting temperature, errors will result due to partial decay of the thermoluminescence before the warm-up is begun; and if the glow peak is below the starting temperature it cannot be seen at all. For example, in a ZnCdS_xAg sample having a zinc-to-cadmium ratio of 2 to 1 a small glow was observed at low temperatures which dropped off rapidly at increasing temperatures; no maximum occurred in the curve.

In order to determine whether silver as a dopant contributes to the formation of trapping states, undoped samples were prepared. No observable differences occurred in their glow curves.

The glow curves of the ZnCdS_xAg films are characterized by having a single peak which is quite broad. Some of these glow curves are shown in Figure 21. The width of the peaks is caused by a continuous "band" of trapping levels. Table 2 shows the distribution of trap depths

for the various sulfide compositions. This distribution of traps was further studied by the use of "decayed" glow curves.

A typical example of a "decayed" glow curve of the sulfide family is shown in Figure 22. After the initial excitation at liquid nitrogen temperature the sample has undergone four warming cycles, each to a higher temperature than the former. This shows the trapping levels to be distributed over a range of 100° C or more. This temperature range corresponds to a range of trap depths of about 0.2 electron volts, which is typical of the sulfide family.

Another group of experiments using the technique of "built-up" glow curves showed that a variation exists in the value of s , the escape factor, as well as in the trap depth of the sulfides. In this technique, samples were excited at -186° C with ultraviolet light for short times so that all the traps were not filled. If traps of all depths have the same probability of capturing an electron, one might reasonably expect that the resulting glow curve would be shifted toward higher temperatures for short exposure times. Such an effect would be expected because some of the electrons released at lower temperatures from the shallower traps would be retrapped in the unfilled deeper traps and subsequently contribute to the glow curve at a higher temperature.

Using a sprayed zinc cadmium sulfide film with the composition ratio of six zinc to one cadmium, UV exposures were made for five seconds with the intensity being varied by decreasing the slit widths on the monochromator with each subsequent exposure. As the exciting radiation was decreased initially, the glow curve shifted to lower temperatures and began to shift back toward higher temperatures only when the amount of excitation was about one-tenth of the full amount. Hoogenstraaten⁽¹⁶⁾

has reported similar results for built-up glow curves in ZnS:Ag , and has shown that such an effect can be explained only by assuming that the shallower traps have a higher probability for capturing an electron than the deeper ones, which implies that the frequency factor varies as well as the trap depth.

As mentioned previously, the ZnCdS:Ag films having ZnS content in the 90-100% range appear to be very susceptible to oxidation during heat treatment and this necessitated the use of the embedded covering techniques described in Section 4.1.2. The oxidation could be detected in three different ways -- thermoluminescence, photoluminescence color, and spectral shift between cathodo- and photoluminescence. First of all, the glow curve peak in the high ZnS content samples occurred at a much lower temperature than the curve of Figure 20 had predicted that it should. In Figure 23 two glow curves are shown for a ZnS film and a $(10\text{ZnS} \cdot \text{CdS})\text{:Ag}$ film which were not embedded during heat treatment. Also in this figure there is a glow curve for a ZnO settled powder sample for comparison. It can be seen that the glow peaks of the sulfides correspond closely to the main glow peak of the ZnO.

The second indication of oxidation was photoluminescence color. The color was not uniform over the surface and there was a definite shift toward longer wavelengths away from the very blue color characteristic of ZnS:Ag phosphors. This color difference was especially pronounced along the sample edge where most of the oxidation would naturally occur. This blue-green color was closest to the characteristic ZnO luminescence.

The third indication of oxidation of the films was the shift in spectral peak between cathodo- and photoluminescence. The cathodoluminescence appeared bluer to the eye and peaked at a shorter wavelength than

the photoluminescence. Photoluminescent spectra of samples containing no cadmium had peaks at wavelengths as long as 520 mμ, while the corresponding cathodoluminescent spectra peaked around 450 mμ. This effect is interpreted as an indication that the oxidation occurs more on the surface of the film. Thus the ultraviolet rays, being strongly absorbed at the surface, produce a luminescence with a much higher green contribution from ZnO than do the cathode rays which penetrate into the bulk of the film.

When ZnS:Ag films were prepared by embedding in ZnS powder during heat treatment, the oxidation was apparently prevented. The characteristic deep blue of ZnS:Ag was obtained and the spectral peak was the same for photo- and cathodoluminescence. Also the low temperature ZnO glow peak was eliminated but another large glow peak of undetermined origin appeared. This glow curve is shown in Figure 24. The smaller peak at -62°C on this glow curve appears to be the characteristic ZnS glow peak since it falls very close to the curve of Figure 23. The large glow peak is perhaps due to an impurity or a nonstoichiometry produced by the presence of the powder in contact with the film.

Further work is needed to produce good ZnS films having the desired color and thickness. The most promising approach at this stage of the development seems to be to spray the film thicker than desired to allow for sublimation, cover with a substrate to prevent contact with powder, and embed this arrangement in ZnS powder to prevent oxidation and to slow down the sublimation of the film.

5.4 Factors Affecting Phosphor Screen Efficiency and Resolution

Luminescent efficiency and resolution are primarily dependent upon aluminum film thickness, phosphor film thickness, and beam voltage.

Feldman ⁽¹⁷⁾ showed that for a given phosphor film, a plot of luminescent brightness as a function of voltage has a maximum at different voltages depending on the thickness of the aluminum film coating; and at sufficiently high voltages, the brightness is greater, the thicker the aluminum film. This effect is caused by scattering of the electron beam in the aluminum, causing a greater percentage of the total beam energy to be absorbed in the phosphor. At higher energies where the electrons pass through the film and into the glass substrate, the total energy absorbed from the electron beam by the phosphor film decreases and thus brightness decreases. At lower beam voltages, all electrons are stopped before penetrating the full thickness of the phosphor, and the brightness is directly proportional to the voltage. Thus maximum brightness occurs for some intermediate beam voltage, the exact value depending on the thicknesses of the aluminum and phosphor films.

Figure 25 shows curves of brightness of a ZnCdS_2Ag phosphor film ($1\ \mu$ thick) as a function of beam voltage for four different thicknesses of aluminum. The beam current density used for these measurements was 10^{-6} amperes/cm². Note the threshold voltage for obtaining luminescence increased as the aluminum thickness increased. The maximum brightness appears to occur between 10-15 kilovolts. The best efficiency would be obtained with the thinnest aluminum and about 10 kilovolts of beam voltage. At higher voltages the efficiency obviously drops off rapidly. At lower voltages brightness is proportional to voltage and efficiency is unaffected.

For a given beam voltage, maximum brightness will occur with a thin aluminum backing and a screen thickness which is just great enough to stop all the electrons.

Another factor contributing to the brightness of the film is

the technique of aluminization. When a thin aluminum film was vacuum evaporated onto the back of the phosphor screen such that the light emitted in the back direction was reflected, the intensity of the luminescent film was nearly doubled. However, in order to obtain this factor of two increase, the phosphor screen had to be covered first with a thin layer of nitrocellulose which was baked away after the aluminum was deposited over it. When the aluminum was deposited directly onto the phosphor, it darkened and became non-reflective, thus producing no increase in brightness.

Resolution (in terms of line pairs per unit length) will also be affected by film thickness. For transparent films in which none of the emitted light is scattered, the limit of the resolution will depend on the amount of scattering of the beam. Ehrenberg and King⁽¹⁸⁾ have shown that when a narrow beam of electrons penetrates into luminescent materials, light is emitted from centers within a sphere whose diameter is about equal to the range of the electrons in the medium. Thus the narrowest line which could be obtained on a screen, with a beam of infinitesimal width and energy such that the electrons just pass through the screen, would have a width about equal to the screen thickness.

For a frosty screen in which the emitted light is scattered, the above considerations are unchanged; but there is the additional loss in resolution from the light scattering. If there is a high degree of volume scattering (as opposed to surface scattering) the loss in resolution will not be as great and a considerable increase in efficiency will result.

One obtains efficiency somewhat then at the expense of resolution but by considering all these factors a satisfactory compromise can be made. In general one can optimize the parameters in the following way:

1. Keep the aluminum as thin as possible while obtaining about 100% reflection.
2. The thickness of the phosphor film should be about equal to the width of the line of the finest resolution desired.
3. The beam voltage should be such that the range of the electrons in the phosphor is about equal to the film thickness.

If one is forced to use a beam voltage so great that the electrons pass through the screen, higher luminescent efficiency can be achieved by using a thicker layer of aluminum to reduce the beam energy by scattering before it enters the phosphor. But for resolution, the thickness of aluminum plus phosphor cannot be greater than stipulated in the second condition above.

5.5 Crystallite Orientation in Cadmium Sulfide Films

Previous NCR studies ⁽⁷⁾ found that certain sprayed films of CdS and CdSe exhibit preferred crystal orientation. The questions explored in this study were whether sprayed luminescent films could be prepared which had preferred crystal orientation, and if so, whether the cathodoluminescent efficiency would be affected by such preferred orientation. Cadmium sulfide was chosen for this study because it can be prepared as a luminescent material and preferred orientation had been previously observed in CdS films.

A series of cadmium sulfide films were prepared by solution spraying. The luminescence of these films was correlated with the crystal orientation and crystallite size as determined from their respective x-ray diffraction patterns. Table 3 contains data for representative samples

of the sprayed CdS films. This table lists the substrate used, the type of solution (whether the chemicals were reagent grade or specially purified and whether a silver dopant was added), the spray rate, the substrate temperature for spraying, the heat treatment, and a description of the luminescent properties, the crystallinity and the crystal orientation.

The x-ray diffraction patterns for these films are sketched in Figure 26 through 35. For randomly oriented, hexagonal CdS crystals the $(10\bar{1}1)$ peak is the most intense. Table 4 lists the heights of the various diffraction peaks relative to the $(10\bar{1}1)$ peak for a randomly oriented sample. The method discussed in Section 4.2.1 was used to determine preferred crystal orientation.

It was observed in general that heat treatment increases the crystallinity of the films and improves the luminescent efficiency, but does not appreciably change the crystal orientation. The luminescence of sample PH-915 increased with heat treatment and it may be seen in Figures 26 and 27 that the diffraction peaks are higher and narrower after heat treatment, showing improved crystallinity.

The substrate material used appeared to influence the crystal orientation. Samples PH-932 and PH-941 were prepared the same except different substrate materials were used. Sample PH-941 (Figure 35) deposited on Pyrex shows a much stronger (0002) preferred orientation than does sample PH-932 (Figure 34) which was deposited on soft glass. The peak widths at half height are approximately the same for these samples, indicating that the crystal perfection and size are not significantly different for these substrates. Strong (0002) preferred orientation was also found on Corning 7056 substrates but the luminescence was very poor.

The substrate temperature during spraying has a significant effect upon crystal orientation. It may be seen in Table 3 and in Figures 28, 29, 31, 32, 34, and 35 that all samples sprayed at 315° C had some preferred orientation. Samples PH-911 and PH-911 HT (Figures 28 and 29) show preferred (1120) orientation and Figures 31, 32, 34, and 35 show preferred (0002) orientation. Those samples prepared at 260° C had approximately random orientation in all cases.

The substrate temperature also has some effect on the crystallinity and luminescent efficiency of the sprayed film before heat treatment. The results with a substrate temperature of 315° C were better than 260° C. However, the substrate temperature during spraying can be too high. A substrate temperature of 370° C caused the luminescent efficiency to be lower than that obtained with a substrate temperature of 315° C.

The difference in level of purity of the solution used and the deliberate addition of 0.025 mole per cent of silver had no effect on the crystal orientation and very little effect on the luminescent efficiency. The luminescent efficiency is generally related to purity, however, purification beyond the reagent grade level of purity had no effect on efficiency in this study. The addition of 0.025 mole per cent silver caused only a small improvement in luminescent efficiency.

The spray rate also had little effect upon the crystal orientation and luminescent efficiency. Samples were prepared with spray rates of 600 milliliters per hour and 200 milliliters per hour. Differences in these samples may be attributed to substrate material and substrate temperature rather than spray rate.

In conclusion, luminescent cadmium sulfide and silver-doped

cadmium sulfide films may be processed so that the (0002) plane is preferentially oriented parallel to the substrate by spraying a solution of high purity components onto a Pyrex substrate maintained at about 315° C using a spray rate of 200 to 600 milliliters per hour. Heat treatment of such a sample improves the crystallinity and the luminescent efficiency. An appropriate heat treatment is 15 minutes at 650° C in nitrogen with the film covered with another substrate as described in Section 4.1.2. The crystal orientation is primarily dependent upon the substrate material and the substrate temperature during spraying. The luminescent efficiency increases with increased crystallite size and/or perfection, which may be induced by an appropriate substrate temperature during spraying (about 315° C) and by post heat treatment. We found no indication of any correlation between crystal orientation and cathodoluminescent efficiency in this study of sprayed CdS films.

6.0 CONCLUSIONS AND FUTURE WORK

The spray process is capable of providing cathodoluminescent phosphor films in situ on suitable substrates. The substrate material must withstand a spray temperature of 300°C and a heat treatment temperature of 600°C to be usable for this process. Glass and ceramic substrates are the most appropriate substrate materials.

Desired dopants may be incorporated in films prepared by this process by adding such dopants to the spray solution. This was demonstrated by preparing samarium-doped cadmium tungstate films. The luminescent spectrum of the $\text{CdWO}_4:\text{Sm}$ films differs from the spectrum of CdWO_4 films in that three additional bands are present. These bands at 565, 610, and 660 mμ are characteristic of samarium-doped phosphors.

In general, the luminescent properties of the phosphor compositions prepared in film form by solution spraying were found to be in agreement with the properties reported in the literature for phosphor powders of like compositions. This is illustrated by the following examples. The temperature dependent cathodoluminescent color of $\text{CdWO}_4:\text{Sm}$, which was observed to be blue-green at -170°C, bluish-white with a tinge of pink at room temperature, and red-orange at +200°C, is in agreement with the data given by Kroger ⁽¹²⁾ for $\text{CaWO}_4:\text{Sm}$. The red, yellow, and green luminescent phases of sprayed " $\text{Zn}_2\text{SiO}_4:\text{Mn}$ " films were in agreement with the observations of Feldman and O'Hara ⁽¹³⁾ in their studies of evaporated Willemite films. The shift of the spectral emission peak for $\text{ZnCdS}:\text{Ag}$ as a function of the mole percent of ZnS in the film was found to be nearly linear and in general agreement with the observations reported by Drozd and Levshin ⁽¹⁵⁾ and as a final example, the shift of the glow peak temperature as a function of the mole percent of ZnS in $\text{ZnCdS}:\text{Ag}$

was observed to be nearly linear and in agreement with the observations of Hoogenstraaten. (16)

The results of our thermoluminescent studies were extended by using both ultraviolet irradiation and electron bombardment to excite the sprayed film samples. The observed increase in glow curve intensity for most samples with electron excitation may be explained by assuming that the electrons are able to excite a greater volume of the sample whereas the ultraviolet irradiation is strongly absorbed and thus excites only that part of the film near the surface. The intensity of certain glow curve peaks relative to other peaks was observed to be greater for UV excitation than for electron excitation; particularly, the -70°C peak in CdWO_4 . This may be accounted for by assuming that the electron trap responsible for the -70°C peak has a higher density near the surface of the film. With strongly absorbed UV excitation the traps near the surface would have a greater effect on the glow curve than with penetrating electron excitation.

From our preferred crystal orientation study we found that luminescent CdS_xAg films may be processed so that the (0002) plane is preferentially oriented parallel to the substrate. The crystal orientation is primarily dependent upon the substrate material used and the substrate temperature during spraying. Heat treatment of the sprayed films improves the crystallinity and the luminescent efficiency. No correlation between crystal orientation and cathodoluminescent efficiency was observed.

Various compromises and trade-offs are required in designing a high resolution, high efficiency phosphor film screen. First, the film should have a high degree of volume scattering to prevent loss of light by piping to the edge of the film. A satisfactory compromise of the

factors affecting efficiency and resolution for such a film screen may be made in the following ways

1. Metallize with as thin a film as possible while obtaining nearly 100% reflection. If an electron beam voltage must be used which causes the electrons to pass through the phosphor film, a higher efficiency can be achieved by using a thicker film of aluminum.
2. The thickness of the phosphor film should be about equal to the width of the line of finest resolution desired.
3. The beam voltage should be such that the range of electrons in the phosphor is about equal to the film thickness.

Work with the solution spray technique for the deposition of cathodoluminescent films is being continued. The particular areas emphasized in the future work will be:

- (a) The preparation of ultraviolet cathodoluminescent films by the NCR solution spray technique having the desired characteristics of high power radiation in the 2500 to 3500 Angstrom range, short persistence, and resistance to electron burn damage.
- (b) The feasibility of preparing cascade or stratified screens using solution sprayed films.
- (c) The possibility of obtaining directionality in the emission from a cathodoluminescent screen.

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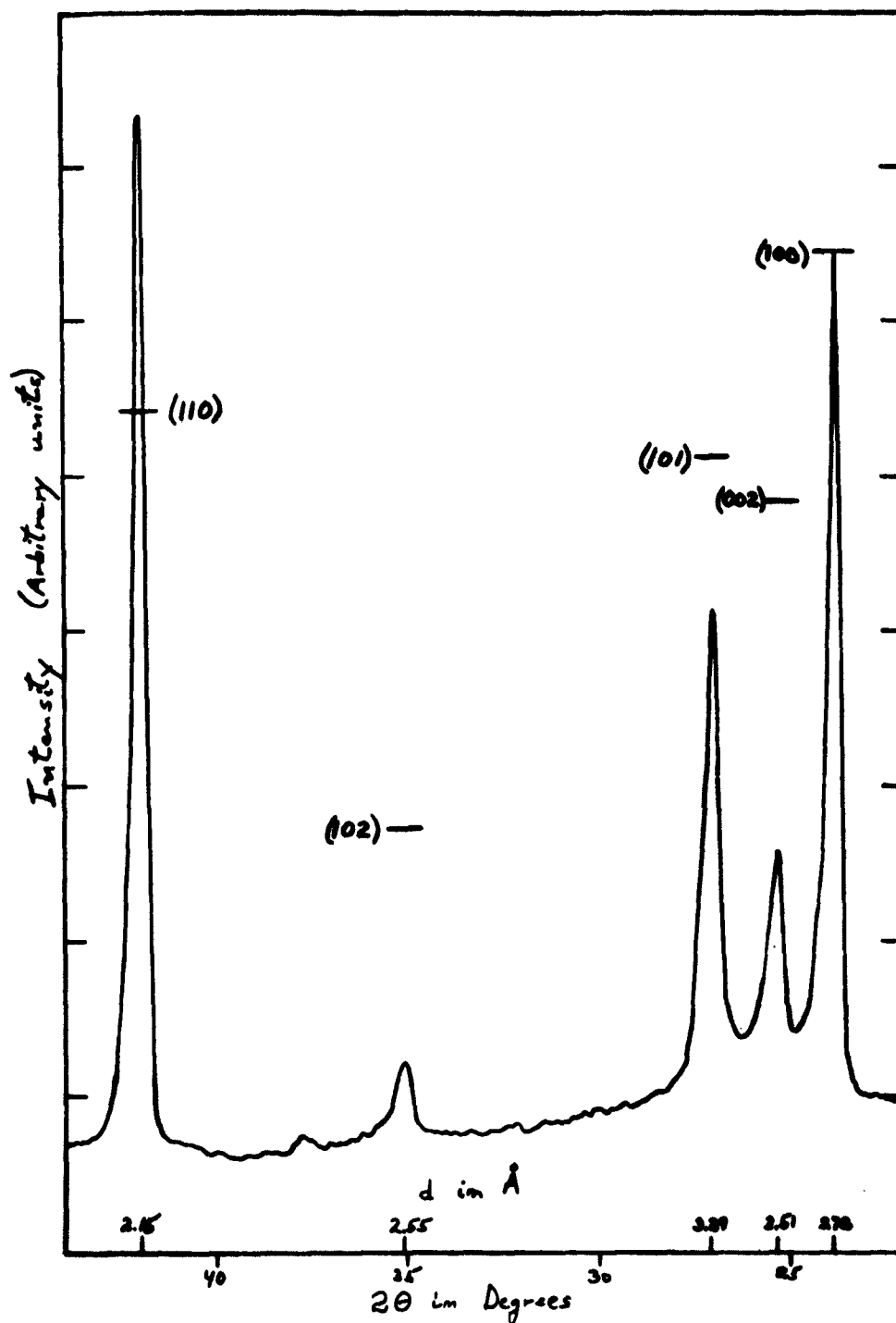


Figure 1 X-ray diffraction pattern of a sprayed CdSe film having preferred crystal orientation with the (110) plane parallel to the substrate. Dashes show the relative peak heights expected for a random crystal orientation.

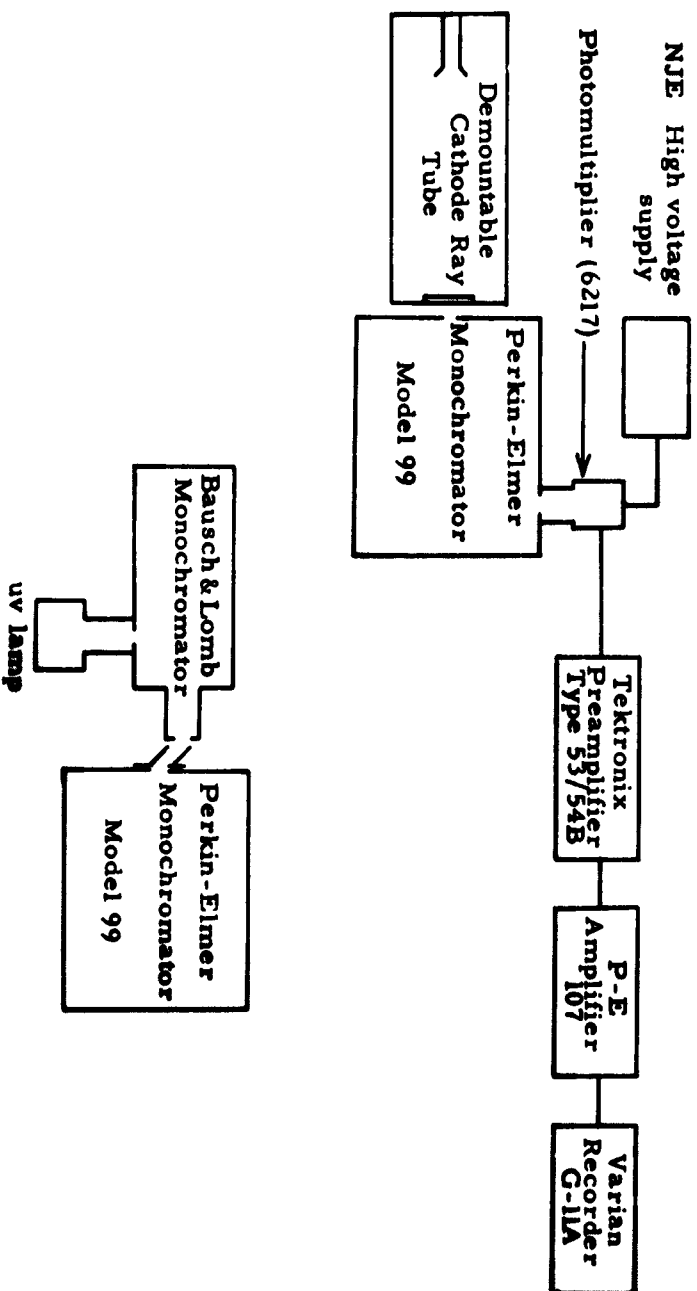


FIGURE 2. SCHEMATIC DIAGRAM OF APPARATUS FOR MEASUREMENT OF LUMINESCENT EMISSION SPECTRA

UPPER: SCHEMATIC FOR CATHODOLUMINESCENT MEASUREMENTS

LOWER: MODIFICATION FOR PHOTOLUMINESCENCE



FIGURE 3. Demountable CRT using 4" x 6" pyrex pipe cross on oil diffusion pumping system

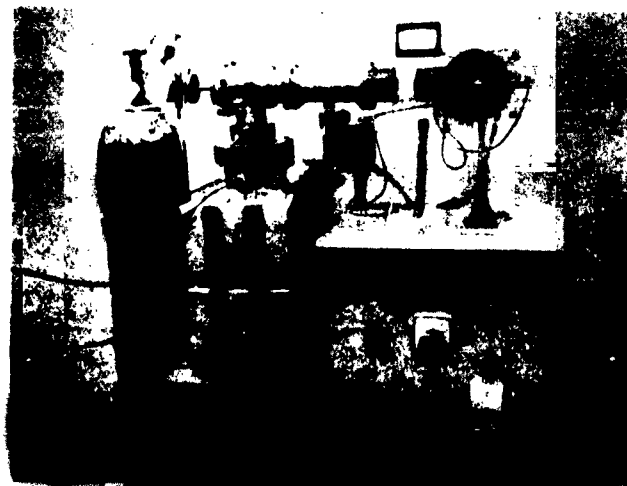


FIGURE 4. Demountable CRT using specially constructed tube on 200 liter/second Ultek ion pump.



FIGURE 5. Specially Constructed Demountable CRT with Quartz Face Plate.

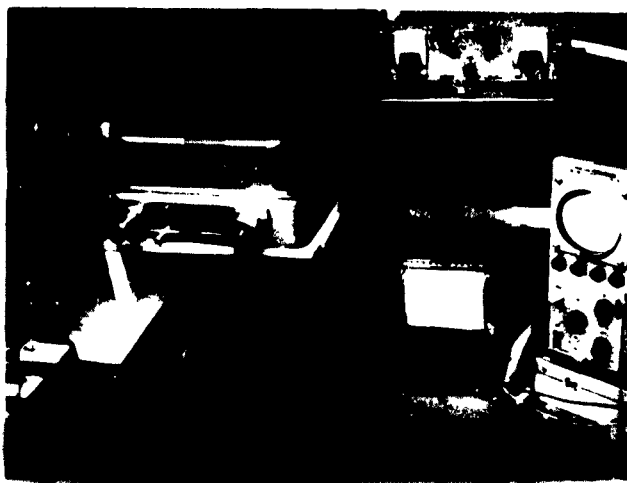


FIGURE 6. Perkin-Elmer Monochromator Positioned and Equipped for Recording Cathodoluminescent Emission Spectra.

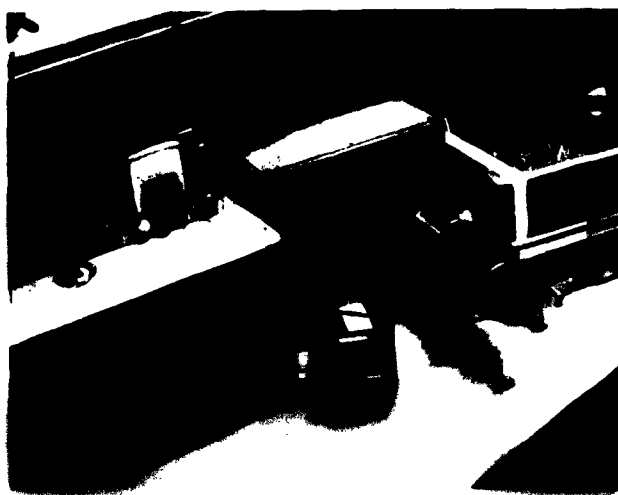
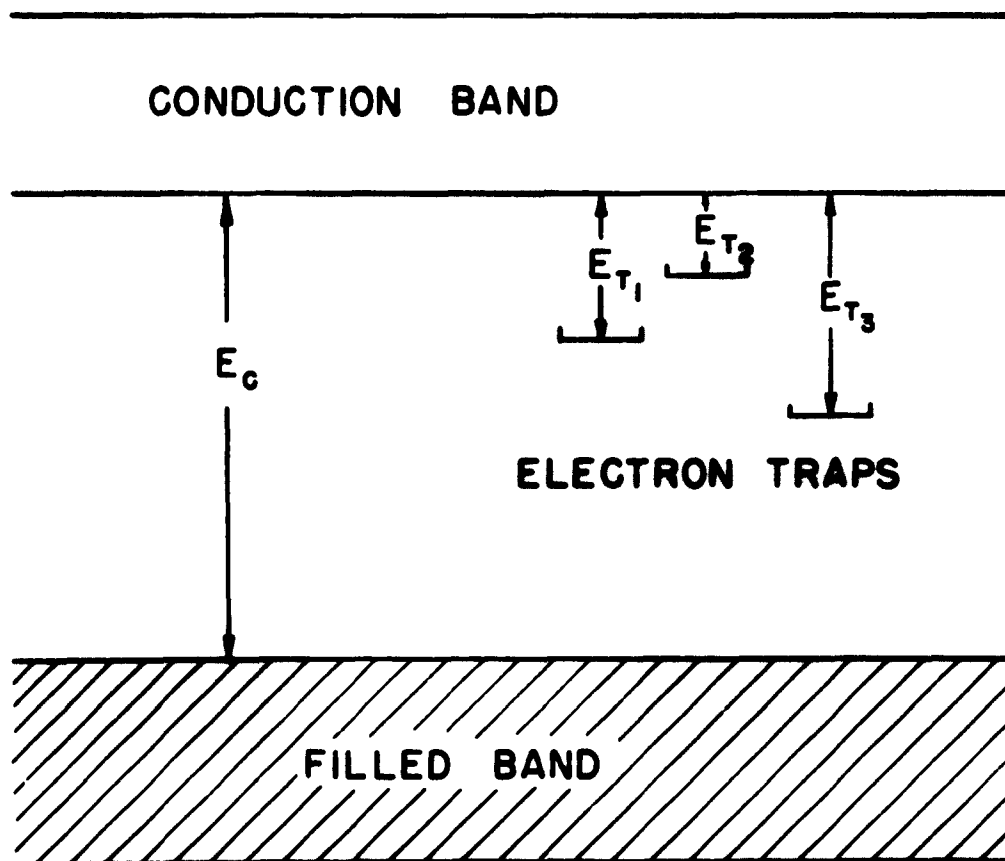


FIGURE 7. Apparatus for Recording Photoluminescent Spectra



FIGURE 8. Glow Curve Apparatus



**FIGURE 9. ELECTRON ENERGY LEVEL MODEL
FOR THERMOLUMINESCENCE**

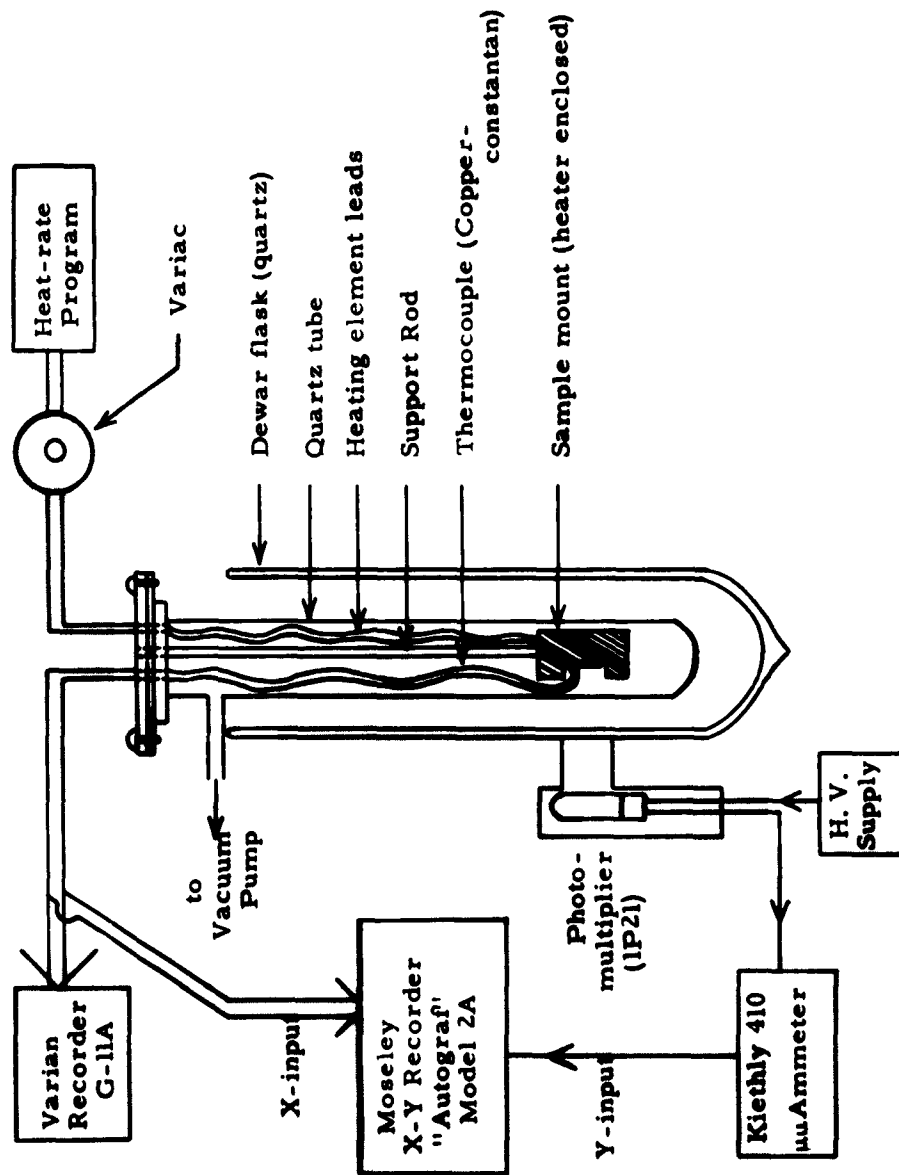


FIGURE 10. SCHEMATIC DIAGRAM OF GLOW CURVE APPARATUS

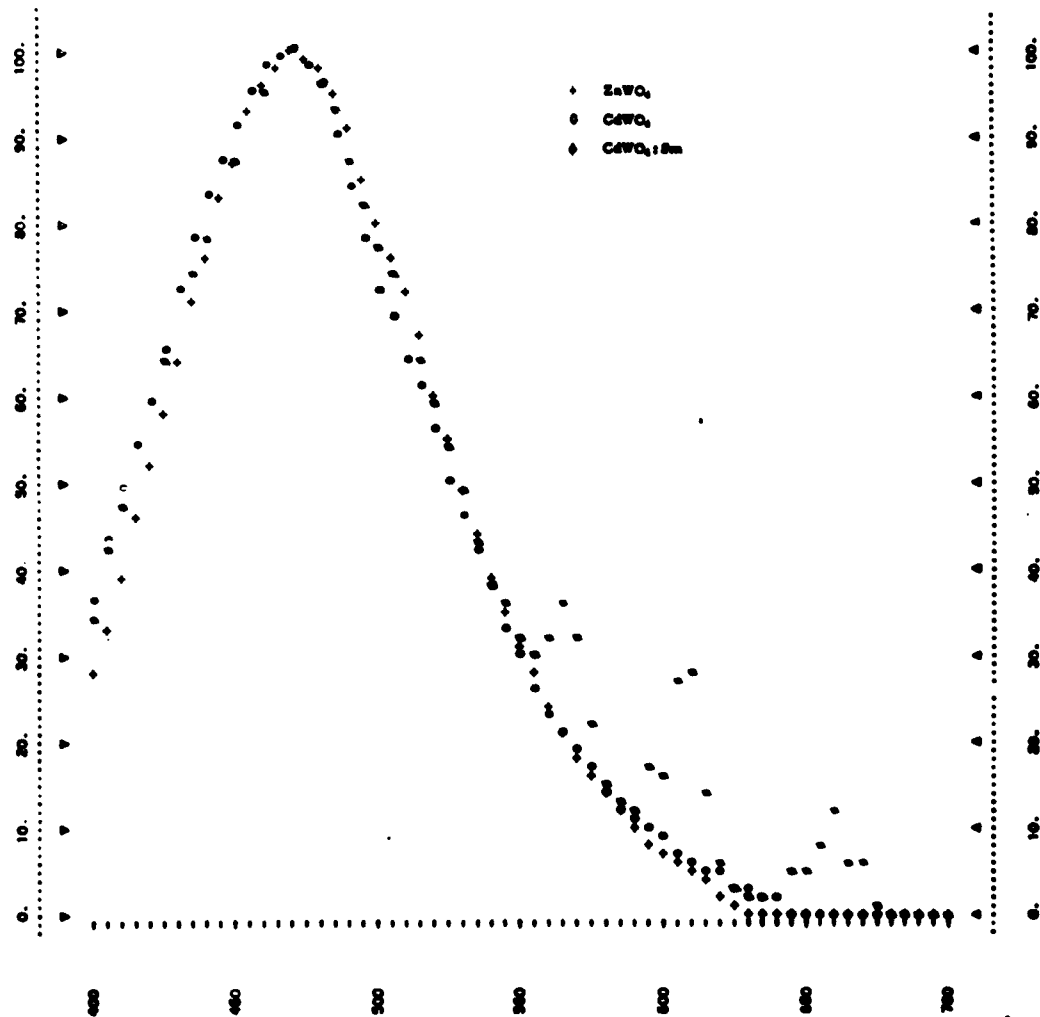


FIGURE 11. NORMALIZED AND CORRECTED PHOTO LUMINESCENT SPECTRA IN RELATIVE UNITS AS A FUNCTION OF WAVELENGTH IN MILLIMICRONS FOR TUNGSTATE SPRAYED FILMS

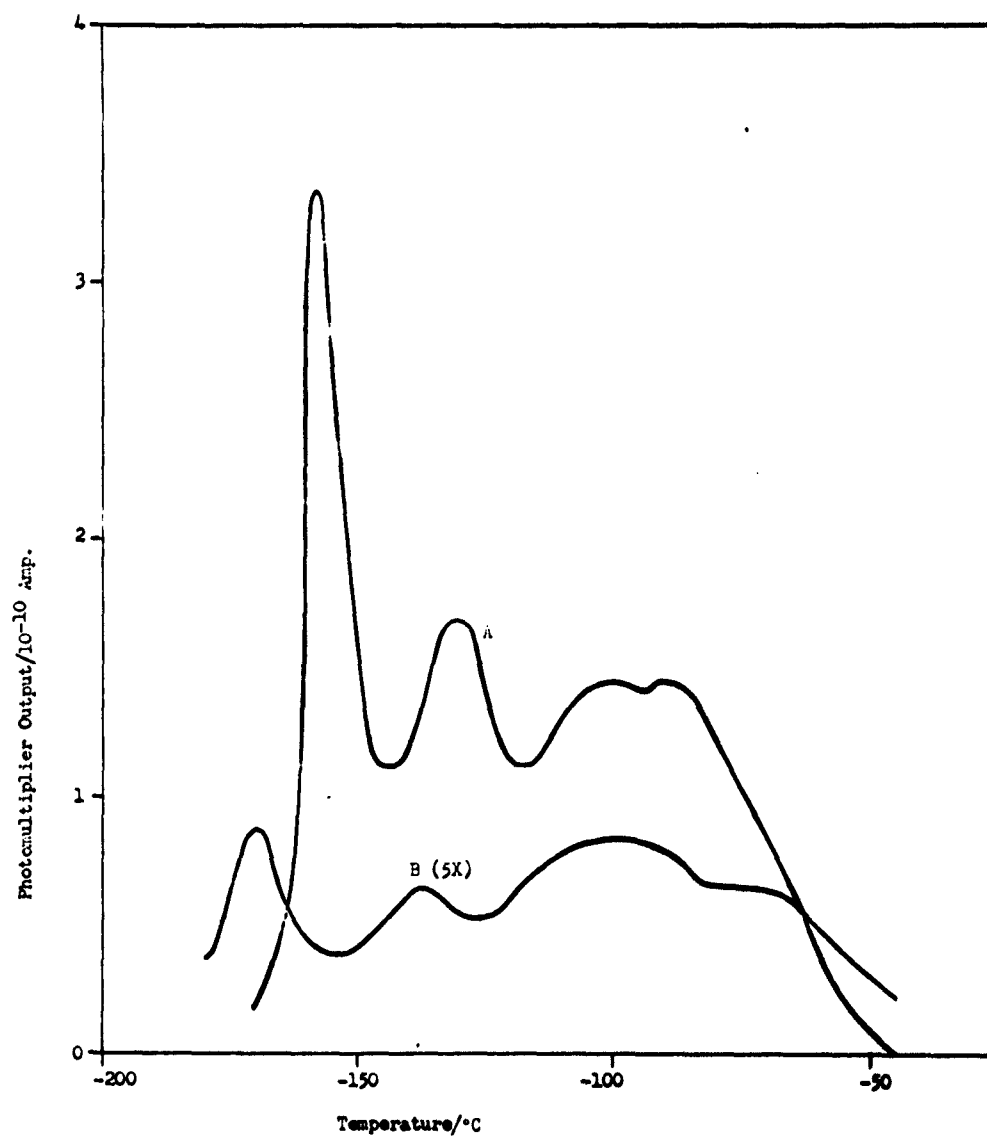


Figure 12 Glow Curves of CdWO_4
 A: Excited by electron bombardment; $\beta = 30^{\circ}\text{C/min}$
 B: Excited by 2537 Å radiation; $\beta = 35^{\circ}\text{C/min}$

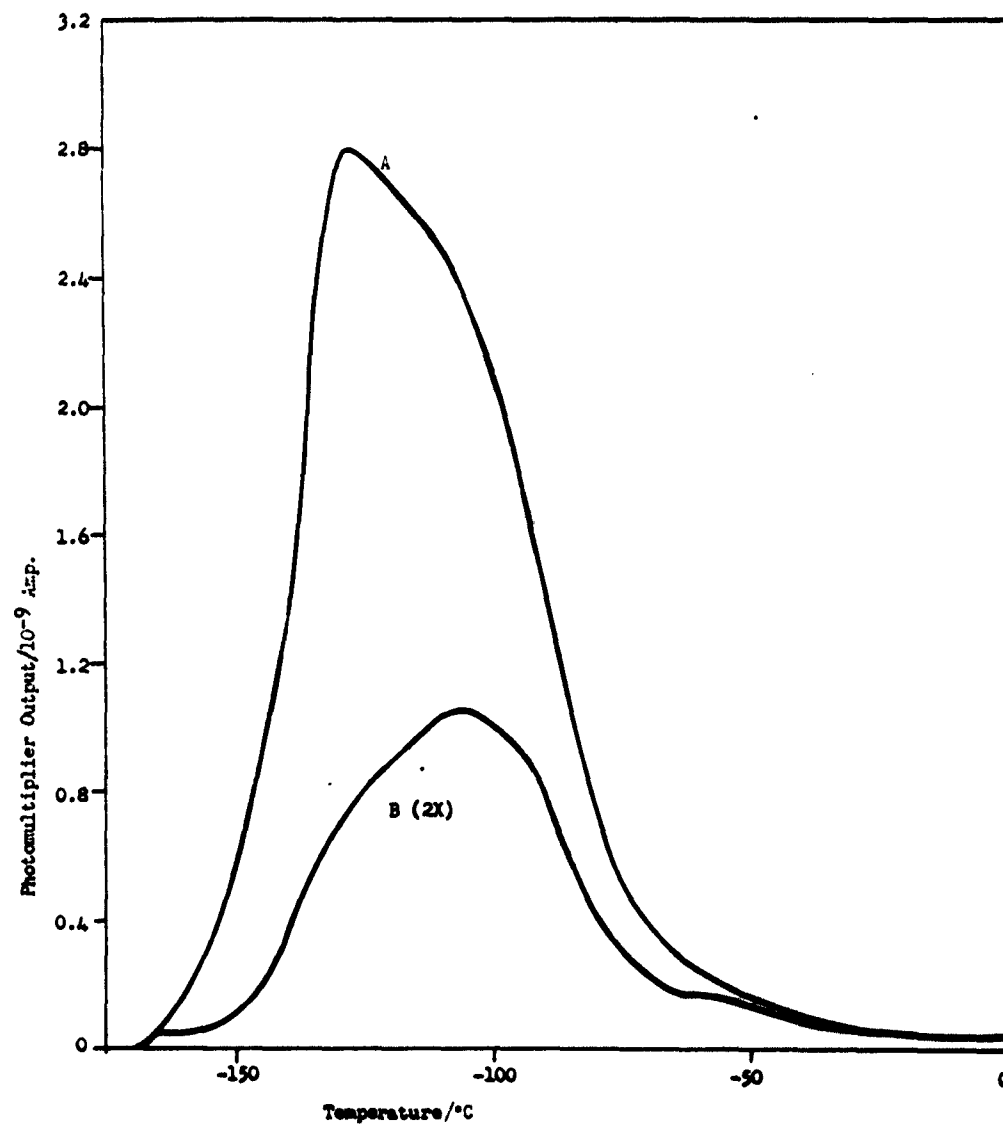


Figure 13 Glow curves of $\text{CdWO}_4:\text{Sm}$
 A: Excited by electron bombardment; $\beta = 35^{\circ}\text{C/min}$
 B: Excited by 2537 Å radiation; $\beta = 30^{\circ}\text{C/min}$

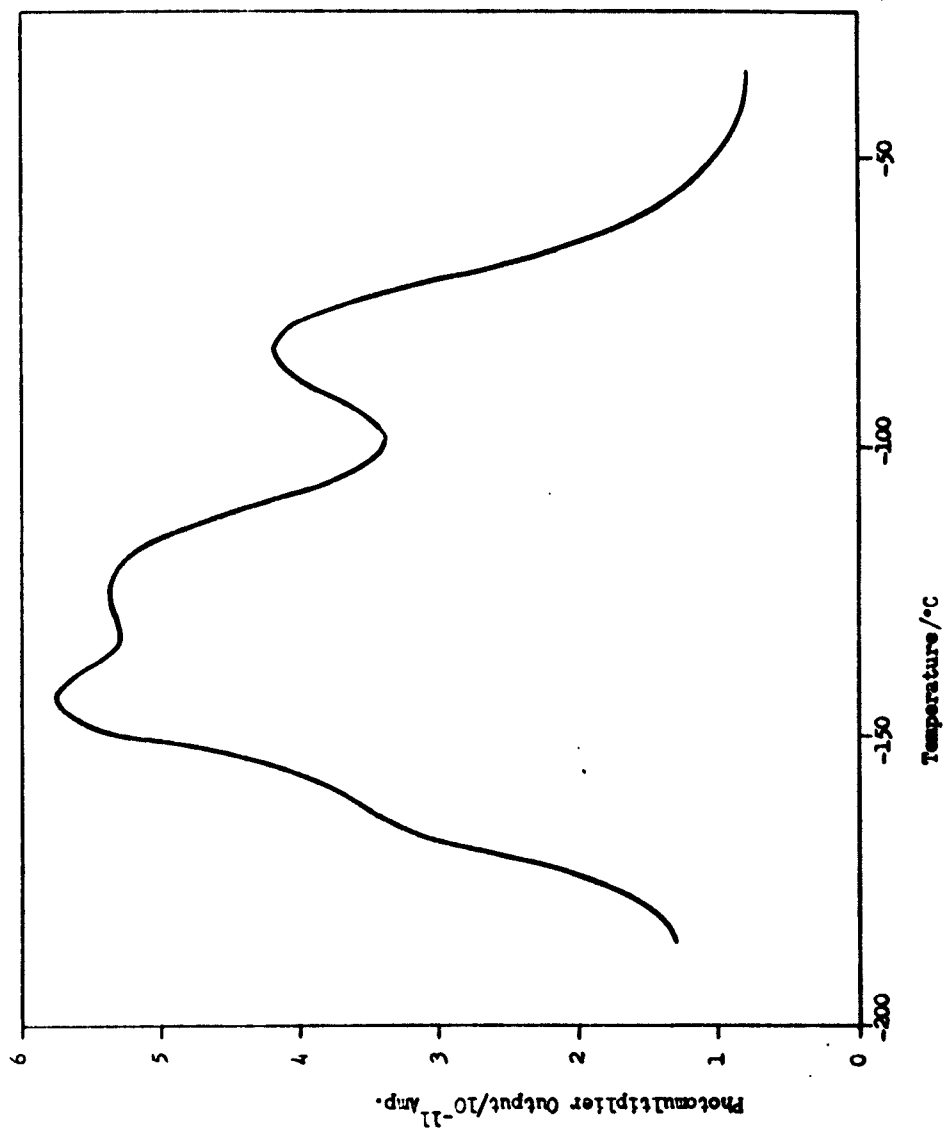


Figure 14: Glow Curve of $\text{CdMoO}_4:\text{Ce}$
 Excited by electron bombardment; $\beta = 38^\circ\text{C}/\text{min}$

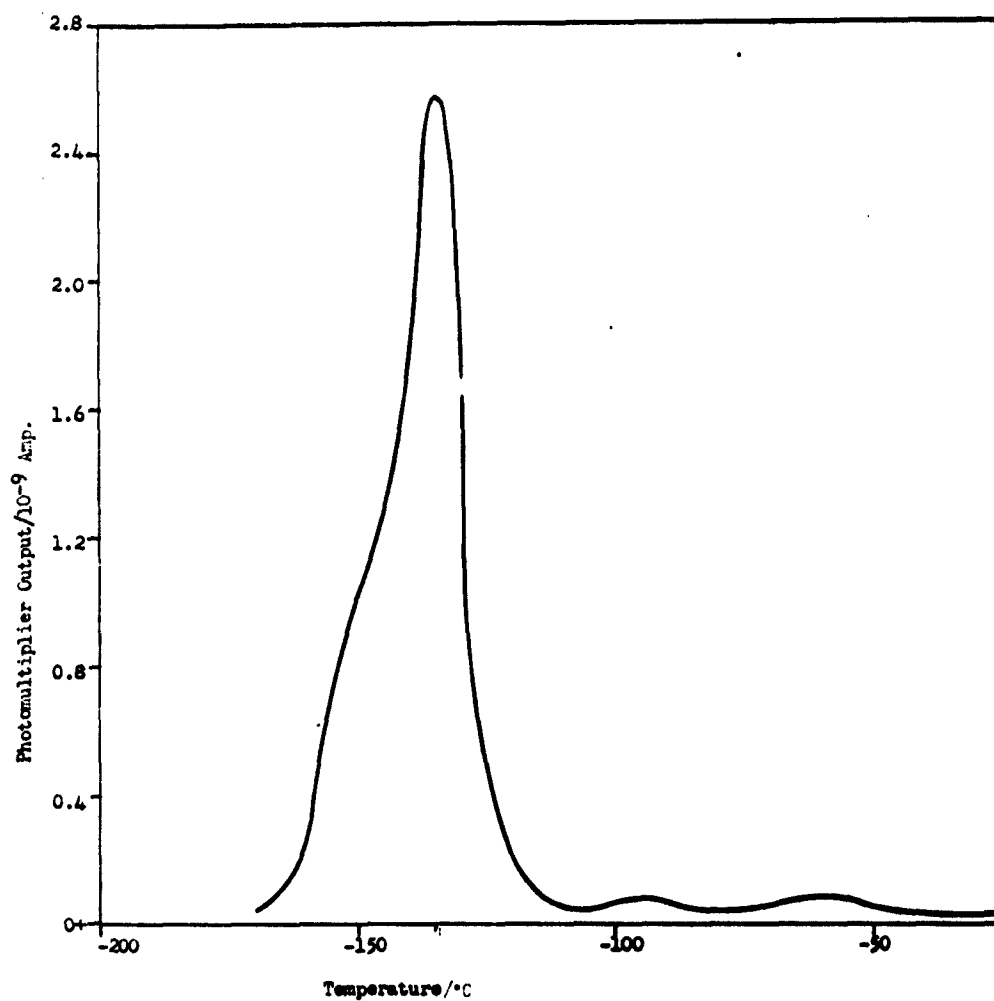


Figure 14: Glow Curve of ZnWO₄
Excited by electron bombardment; $\beta = 25^\circ\text{C/min}$

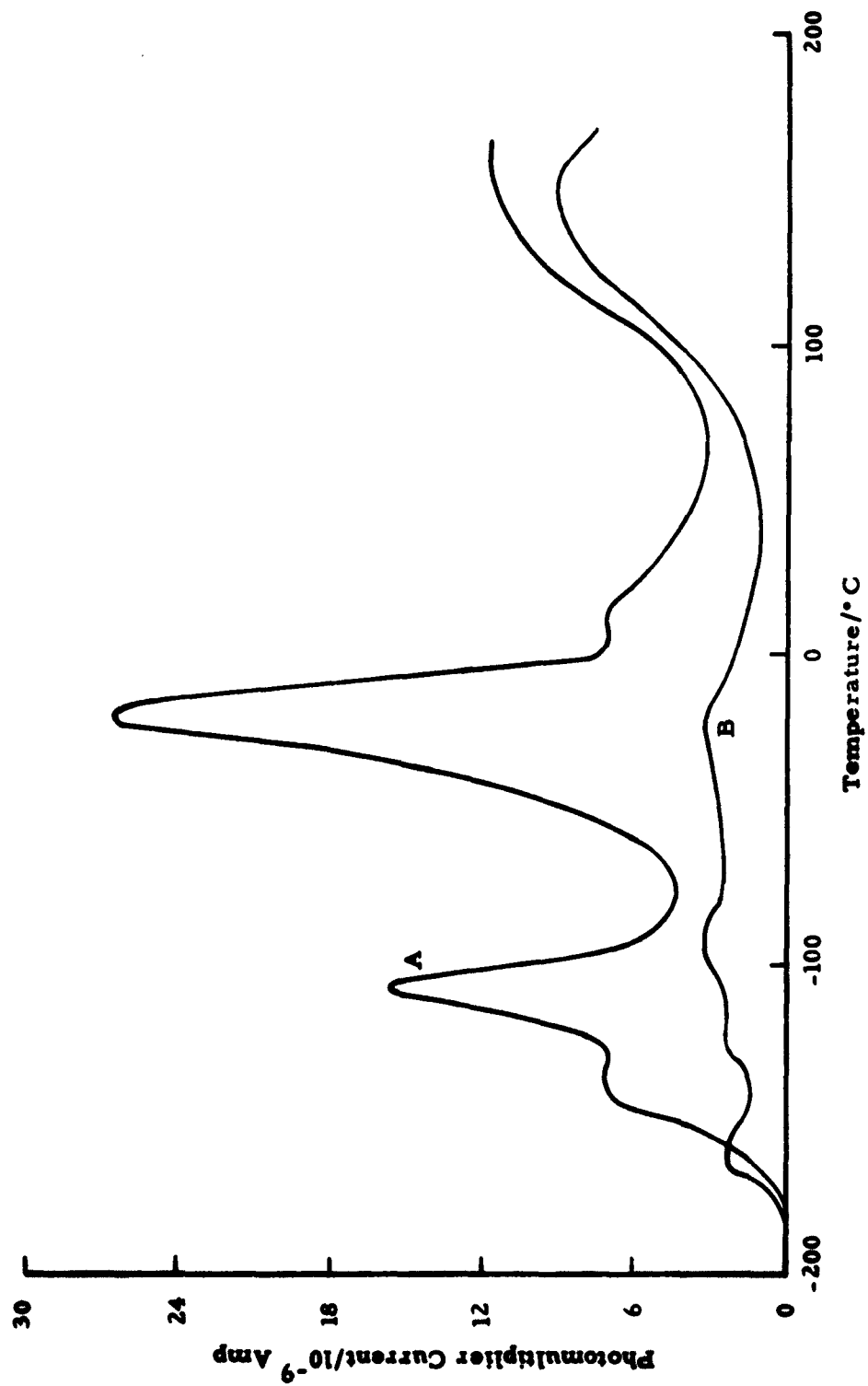


FIGURE 16. GLOW CURVES OF $\text{Zn}_2\text{SiO}_4:\text{Mn}$

(A) GREEN PHASE, WARMING RATE = $12^\circ\text{C}/\text{Min}$.
 (B) YELLOW PHASE, WARMING RATE = $15^\circ\text{C}/\text{Min}$.

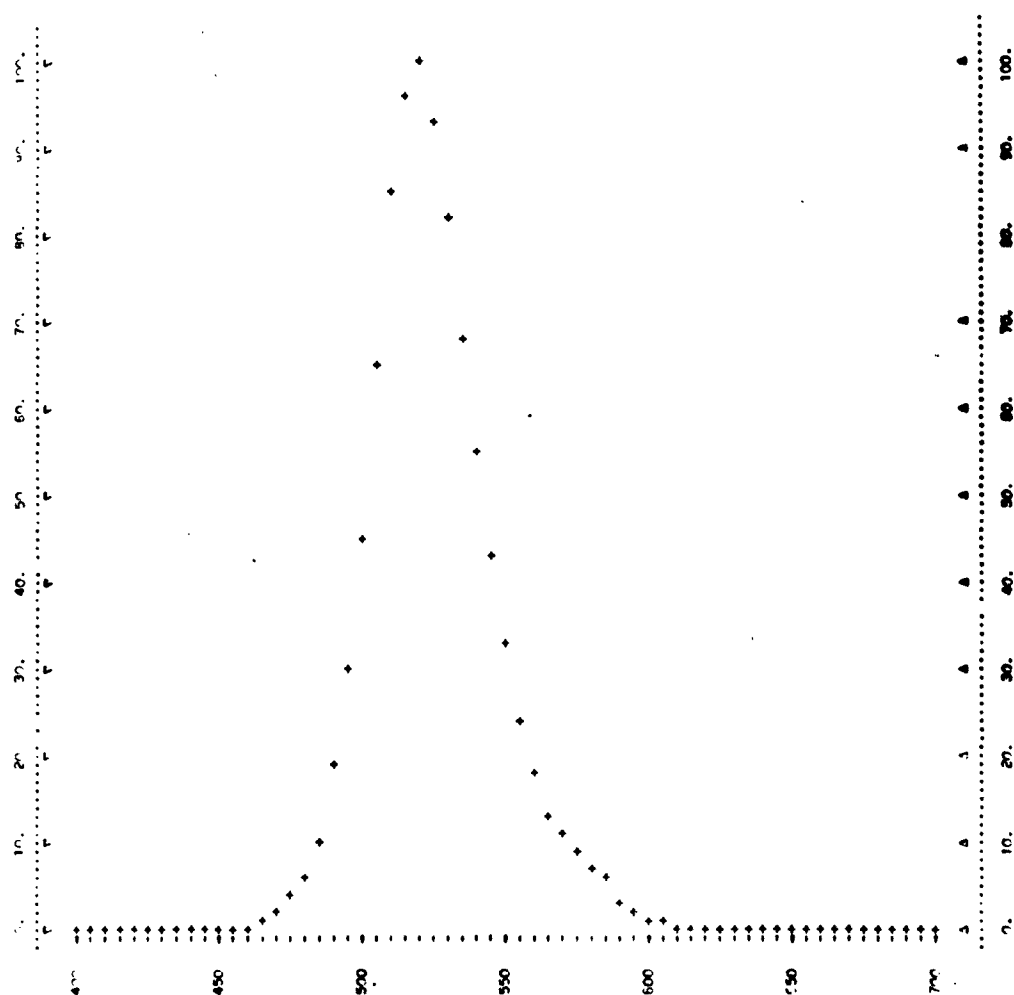


FIGURE 17 NORMALIZED AND CORRECTED PHOTOLUMINESCENT SPECTRUM IN RELATIVE UNITS AS A FUNCTION OF WAVELENGTH IN MILLIMICRONS FOR Zn_2SnO_4 SPRAYED FILM

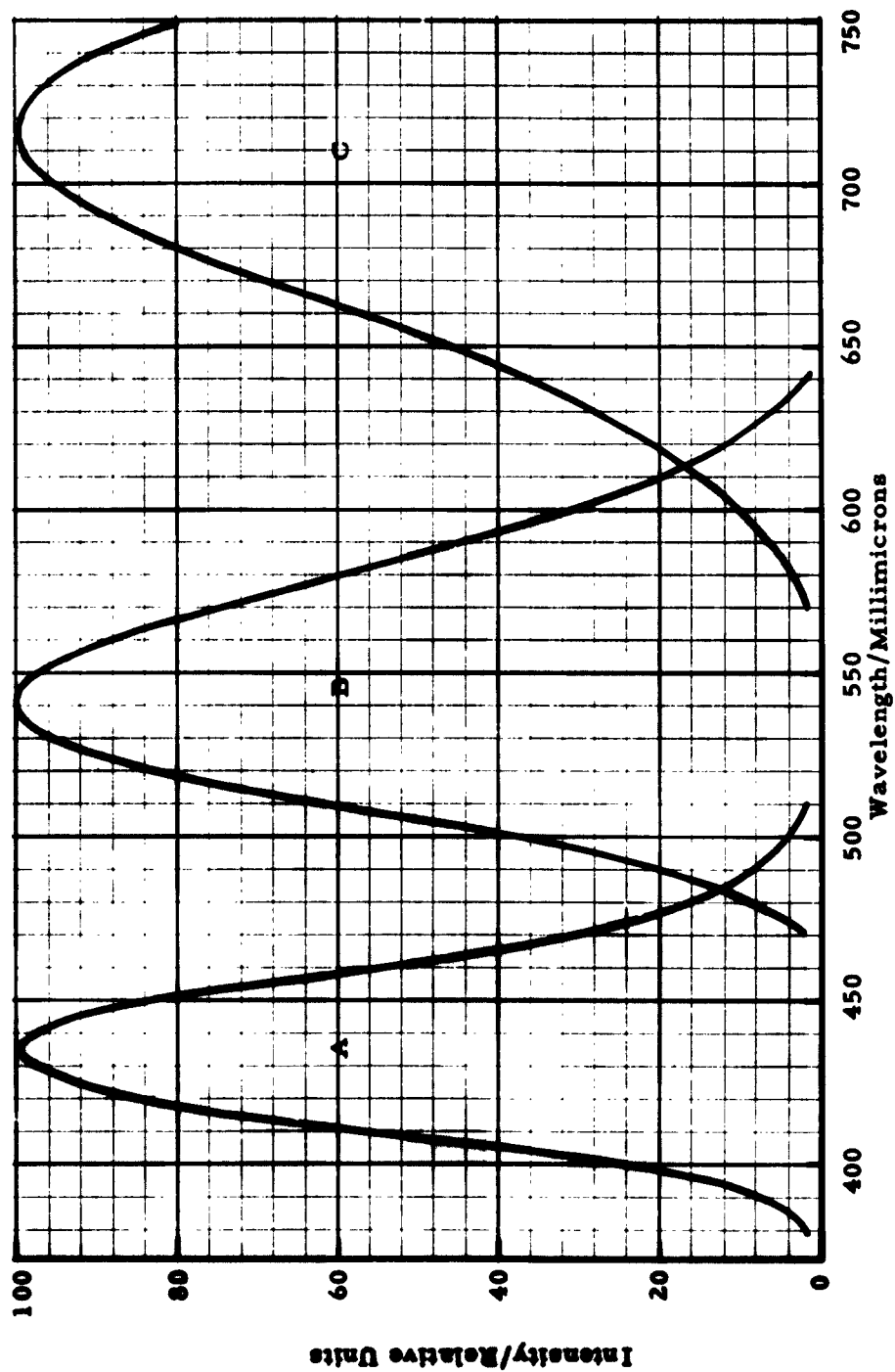


FIGURE 18. LUMINESCENT EMISSION SPECTRA OF:

- (A) ZnS:Ag
- (B) ZnCdS:Ag
- (C) CdS:Ag

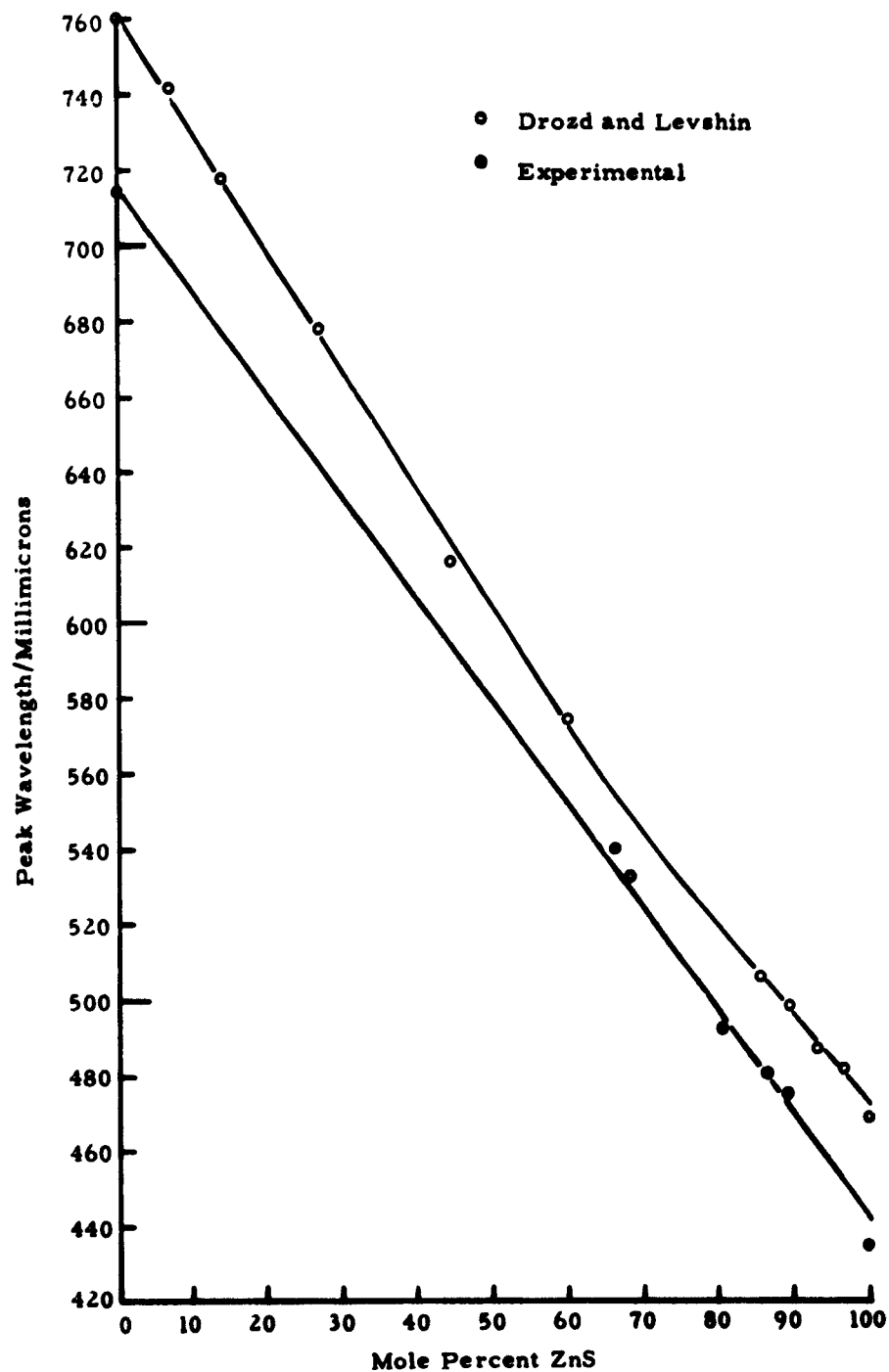


FIGURE 19. PEAK WAVELENGTH OF LUMINESCENCE IN ZnCdS:Ag AS A FUNCTION OF MOLE PERCENT ZnS.

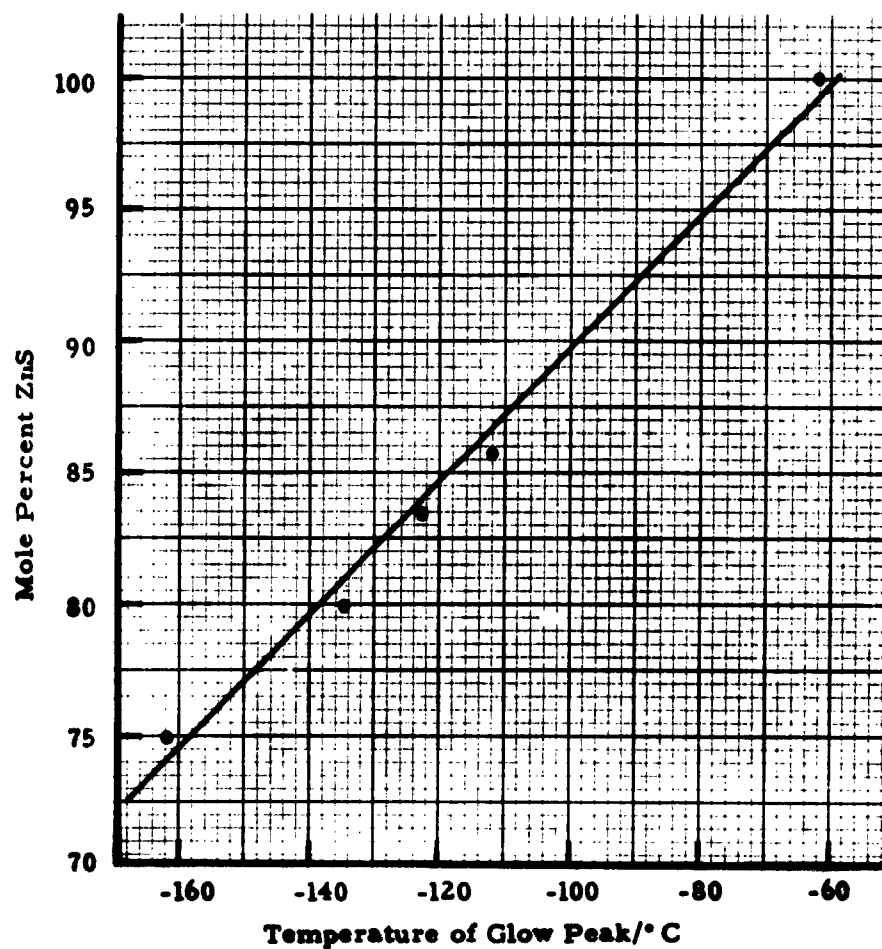


FIGURE 20. TEMPERATURE OF THERMOLUMINESCENCE GLOW PEAK IN ZnCdS:Ag SPRAYED FILMS AS A FUNCTION OF MOLE PERCENT OF ZnS.

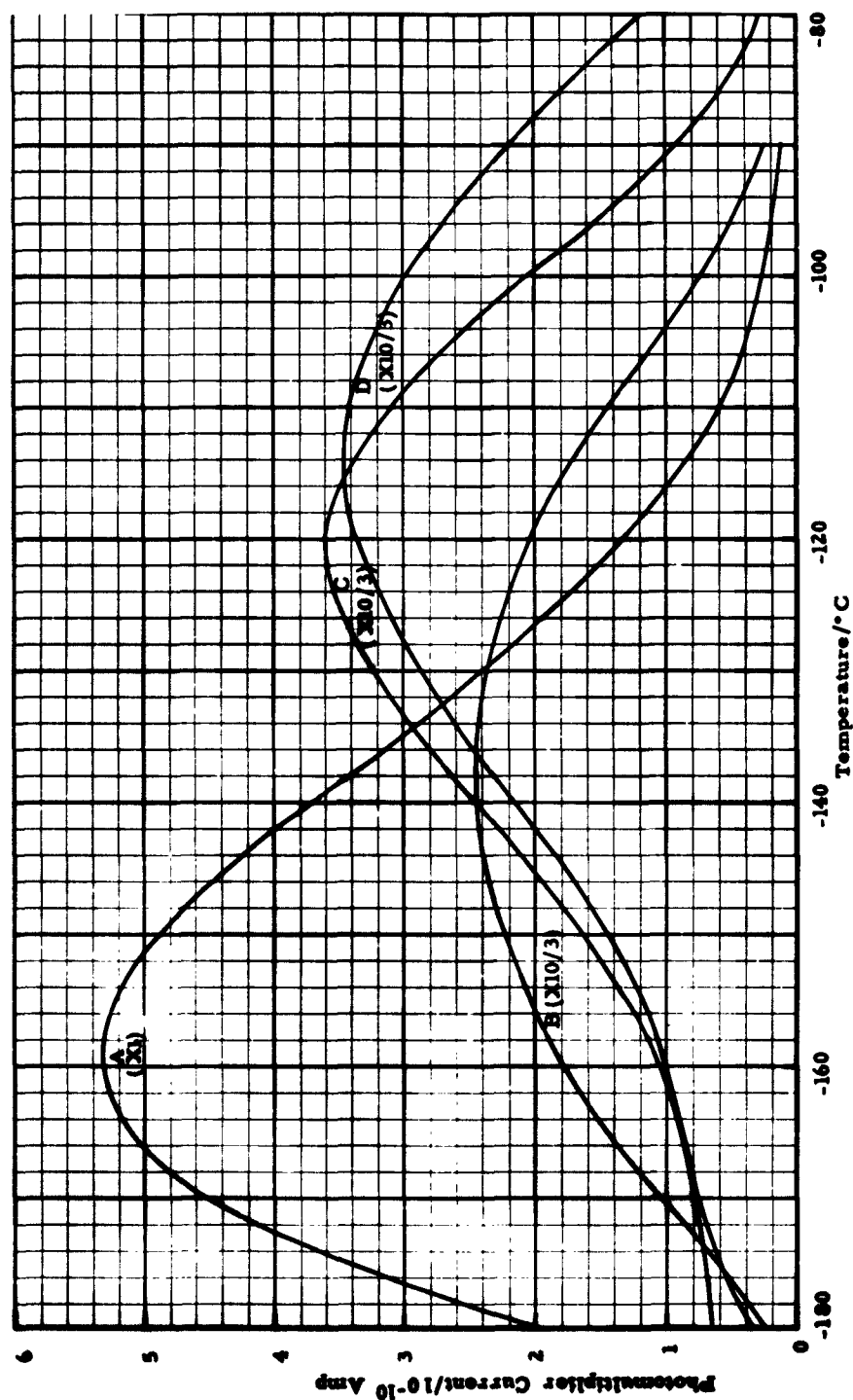


FIGURE 21. GLOW CURVES OF ZnCdS:Ag SPRAYED FILMS WITH VARYING RATIOS OF ZINC TO CADMIUM

- (A) (3ZnS·CdS):Ag, warming rate = 12.5° C/min.
 (B) (4ZnS·CdS):Ag, warming rate = 11° C/min.
 (C) (5ZnS·CdS):Ag, warming rate = 12.5° C/min.
 (D) (6ZnS·CdS):Ag, warming rate = 13° C/min.

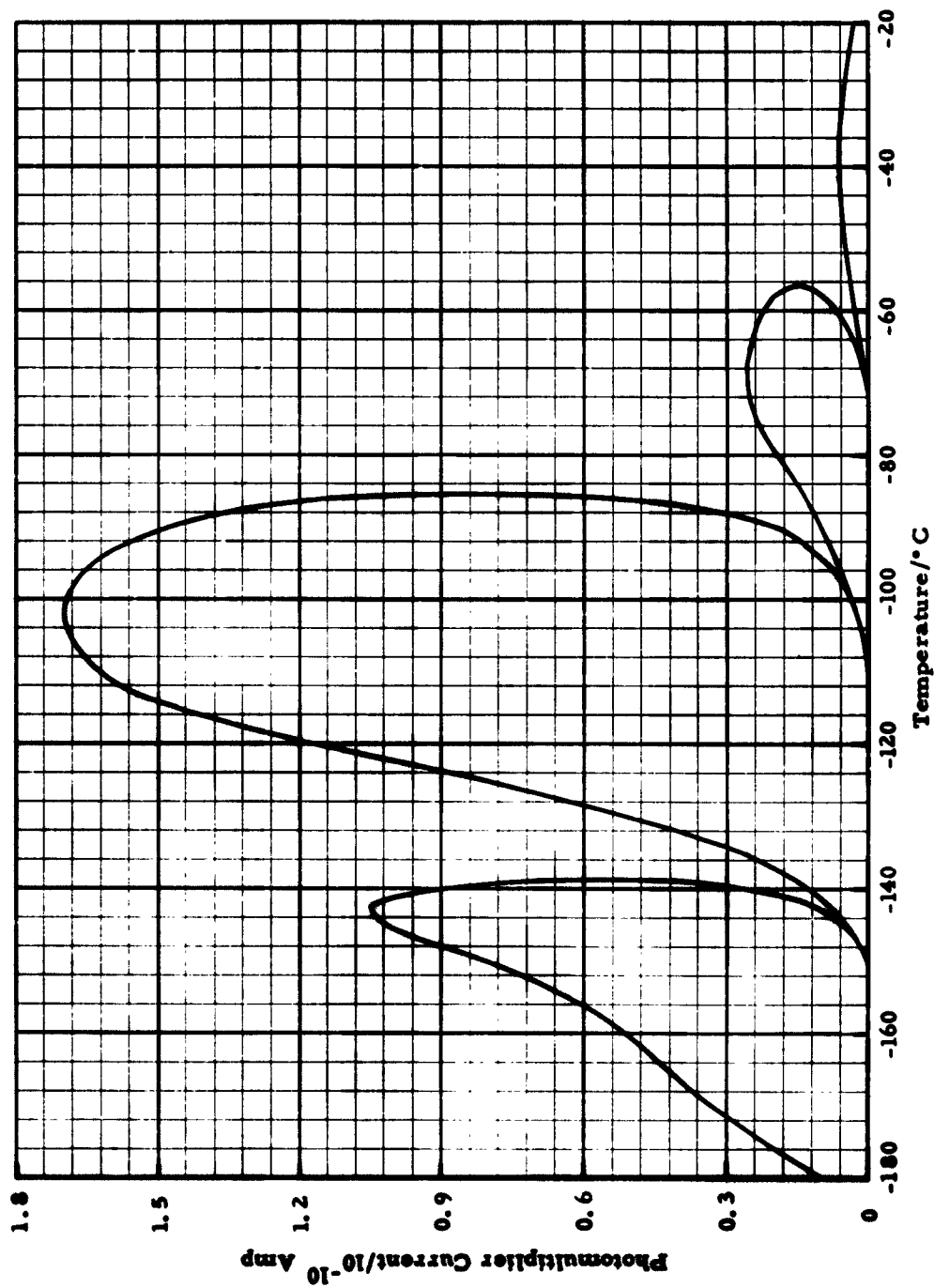


FIGURE 22. "DECAYED" GLOW CURVE OF (6ZnS·CdS):Ag SPRAYED FILM PHOTOEXCITED WITH 3650 Å LIGHT, WARMING RATE = 13°C/min.

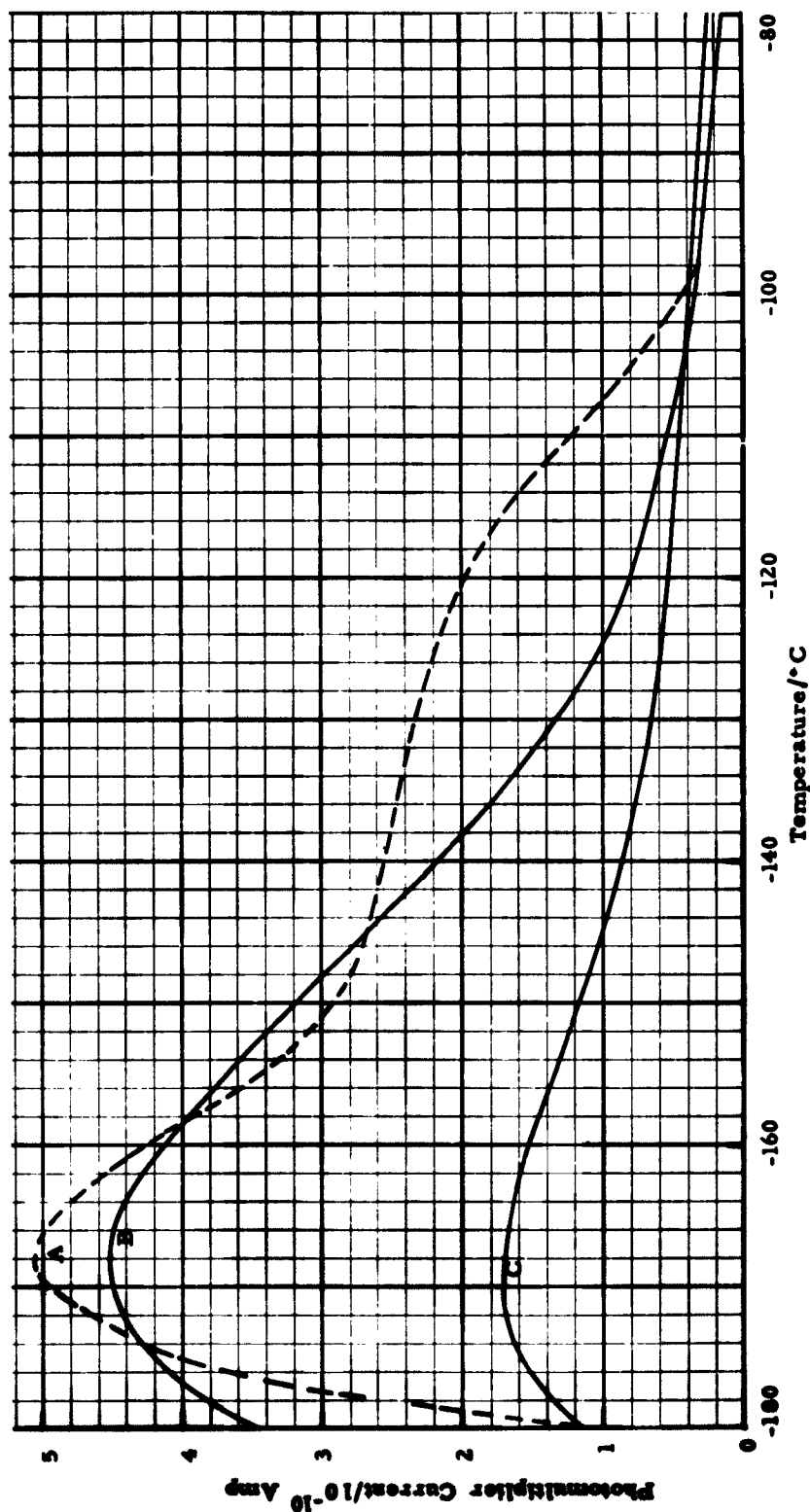


FIGURE 23. GLOW CURVES SHOWING EFFECTS OF OXIDATION
 (A) ZnO Powder, warming rate = $13^{\circ}\text{C}/\text{min}$.
 (B) ZnS Sprayed Film, warming rate = $13^{\circ}\text{C}/\text{min}$.
 (C) $(10\text{ZnS}\cdot\text{CdS})_{\text{Ag}}$ Sprayed Film, warming rate = $13^{\circ}\text{C}/\text{min}$.

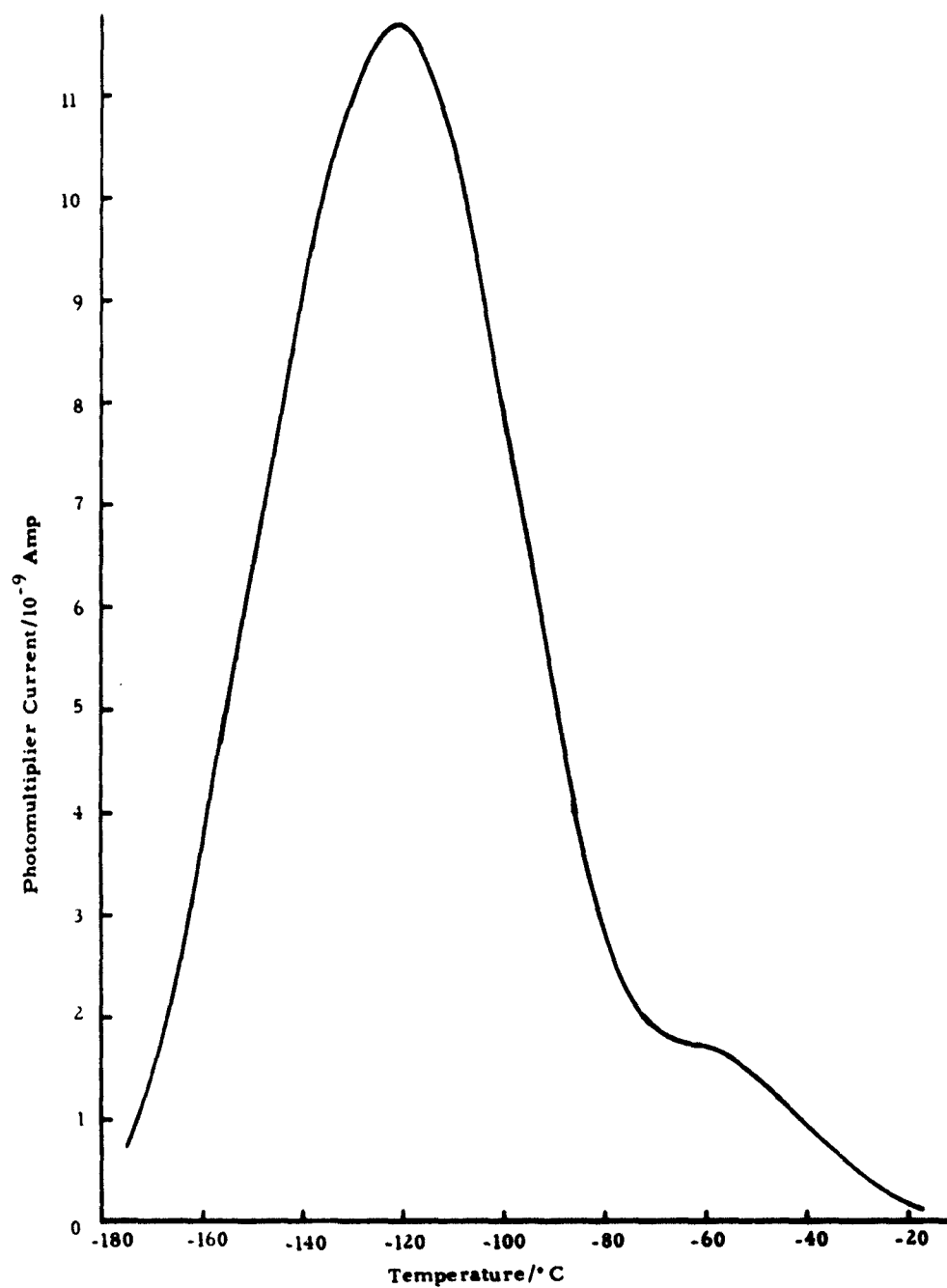


FIGURE 24. GLOW CURVE OF ZnS:Ag SPRAYED FILM,
WARMING RATE = 13° C/min.

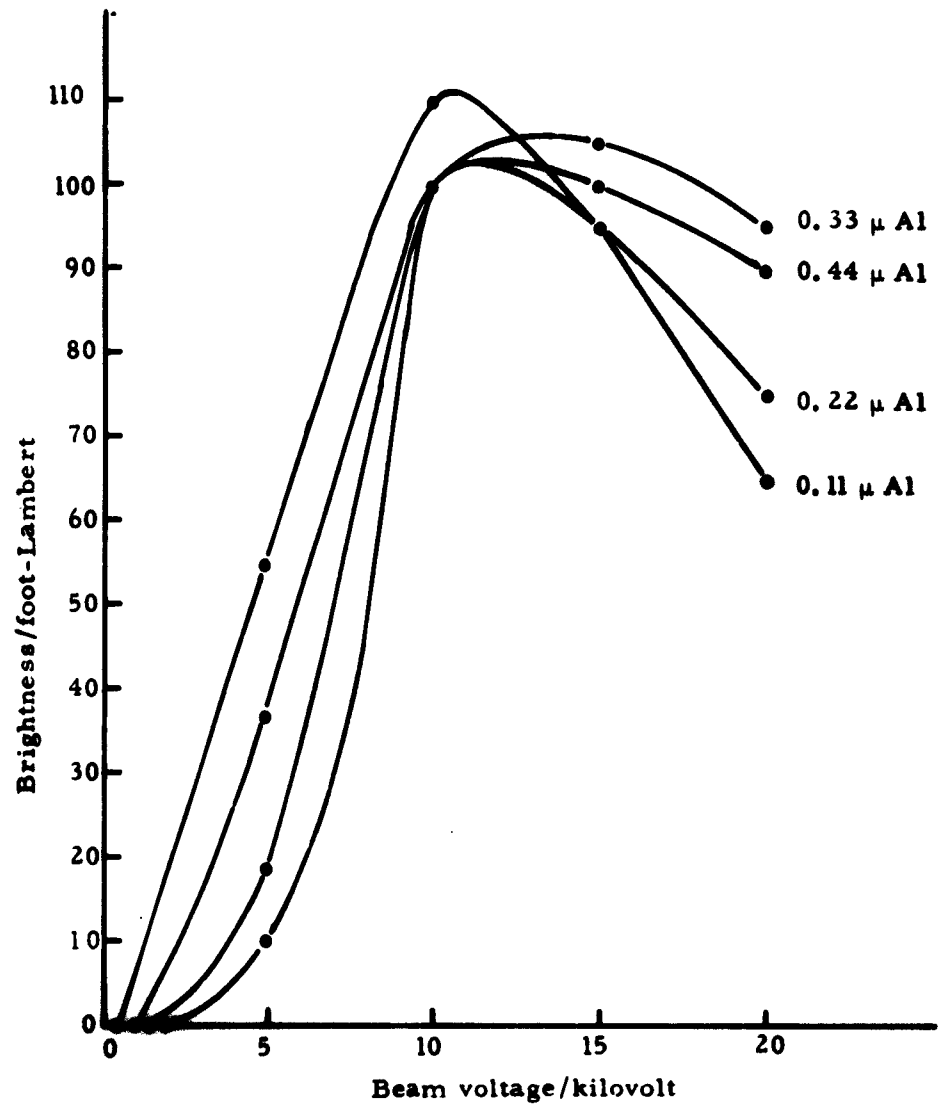


FIGURE 25. BRIGHTNESS VERSUS BEAM VOLTAGE OF A (2ZnS·CdS)₁Ag SPRAYED FILM (1 μ thick) WITH VARIOUS THICKNESSES OF ALUMINUM

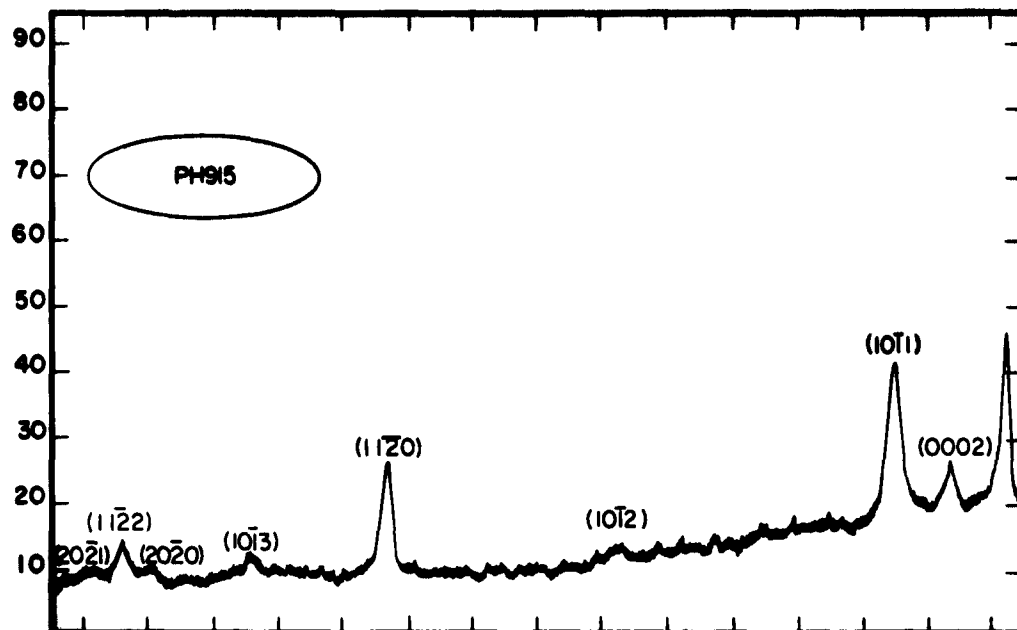


FIGURE 26 - CdS Film Sprayed at 600 ml/hr. Using Reagent-Grade Chemicals; Sprayed on Soft Glass Substrate at 260°C; Poor Luminescence.

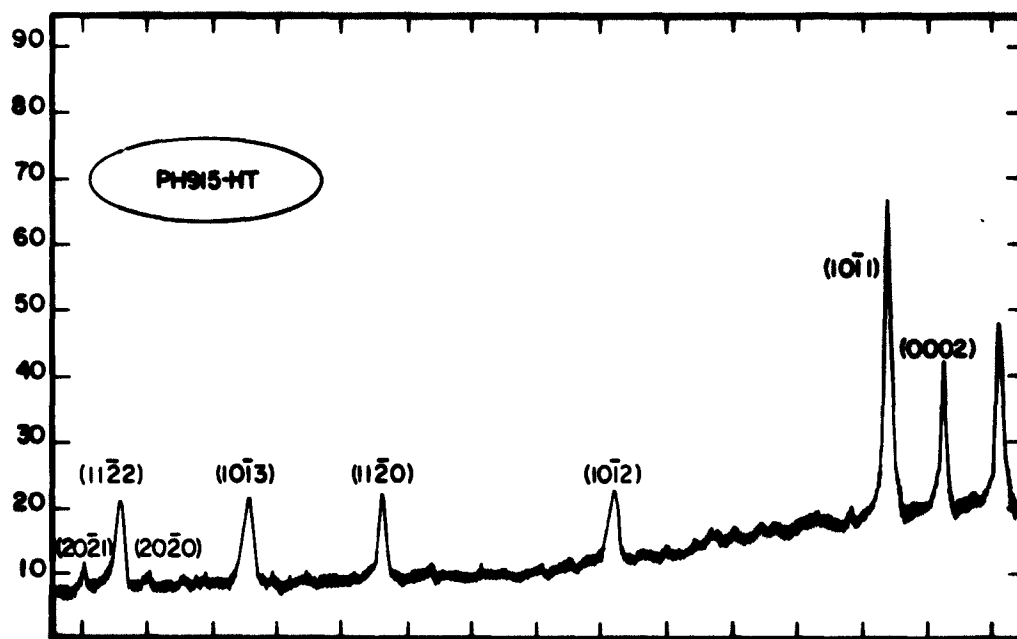


FIGURE 27 - Same as Above except Heat Treated at 650°C; Fair Luminescence

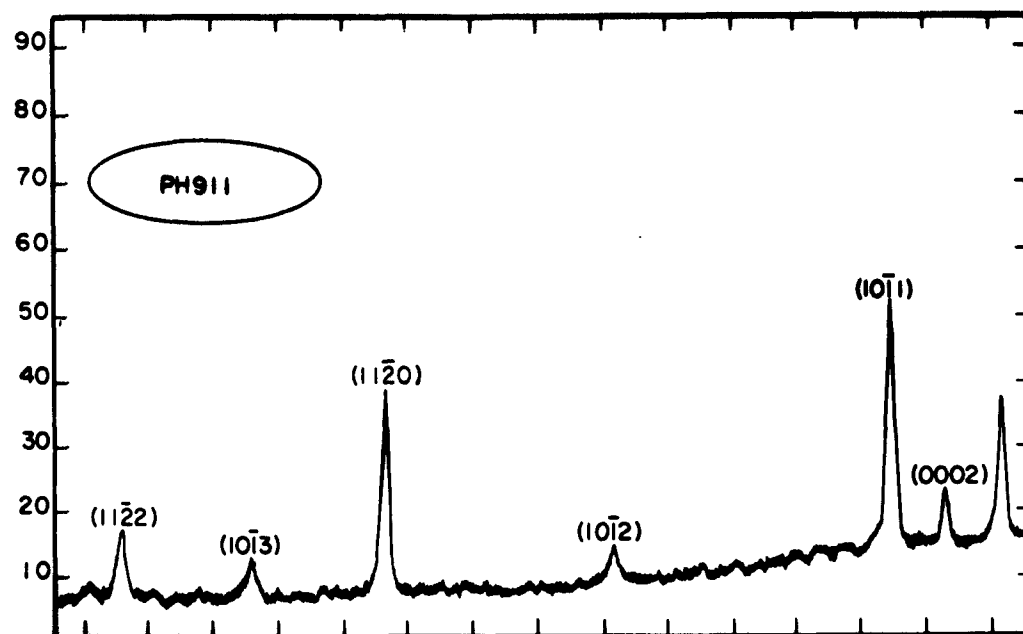


FIGURE 28 - CdS:Ag Film Sprayed at 600 ml/hr. Using Reagent-Grade Chemicals; Sprayed on Soft Glass Substrate at 315°C; Fair Luminescence

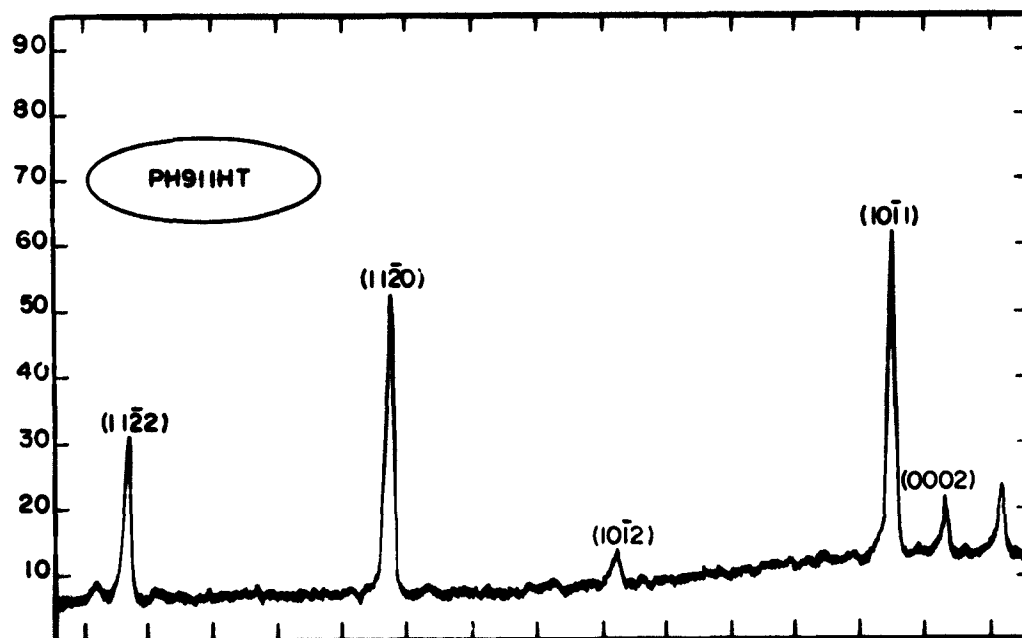


FIGURE 29 - Same as Above except Heat Treated at 650°C; Good Luminescence

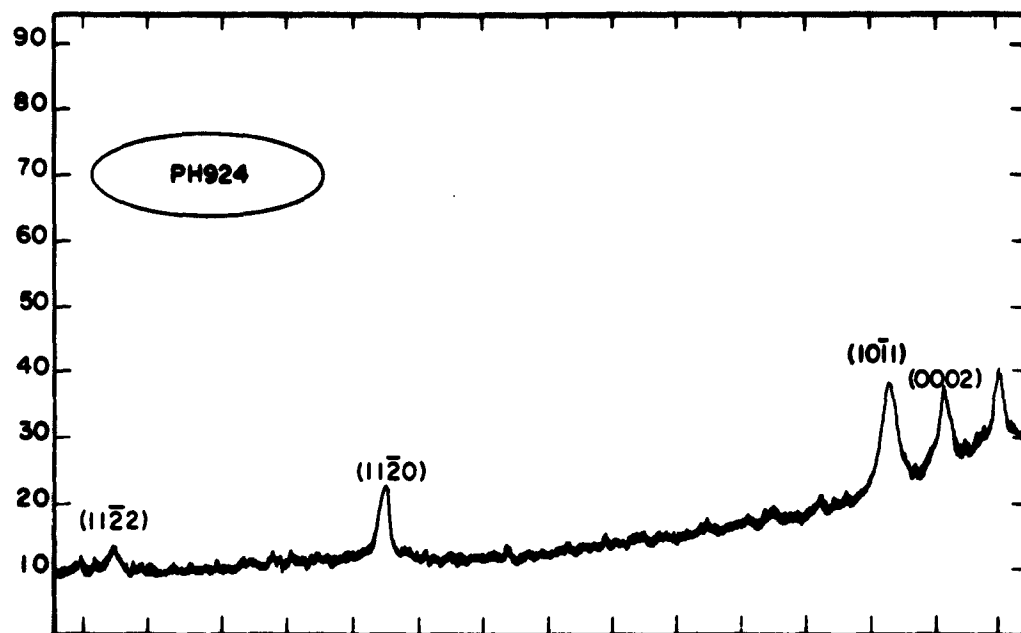


FIGURE 30 - CdS Film Sprayed at 600 ml/hr. Using Purified Chemicals; Sprayed on Pyrex Substrate at 260°C; Very Poor Luminescence.

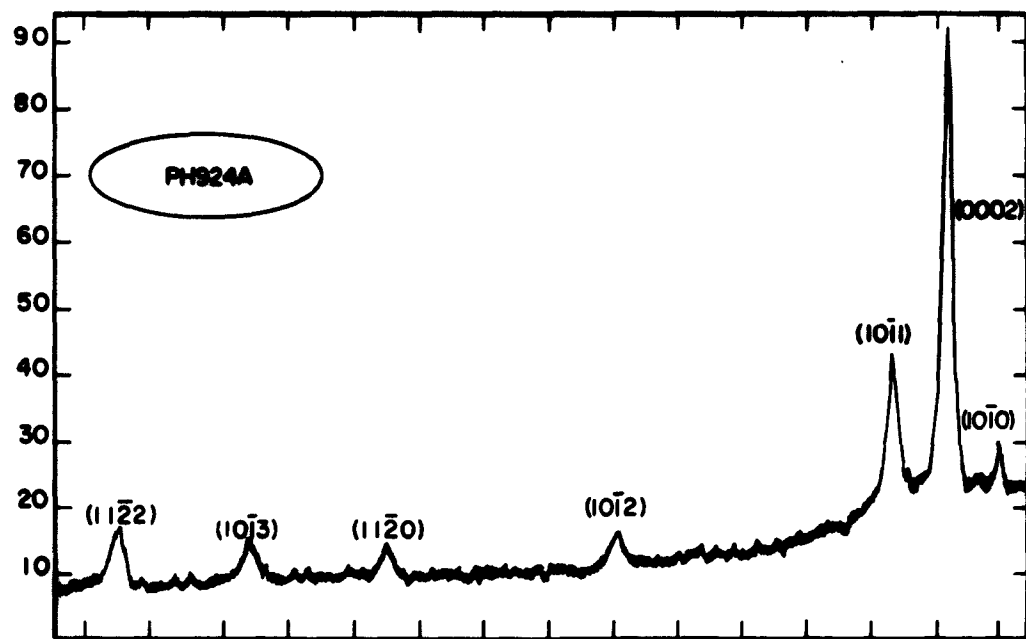


FIGURE 31 - CdS Film Sprayed at 600 ml/hr. Using Purified Chemicals; Sprayed on Corning 7056 Glass Substrate at 315°C; Very Poor Luminescence.

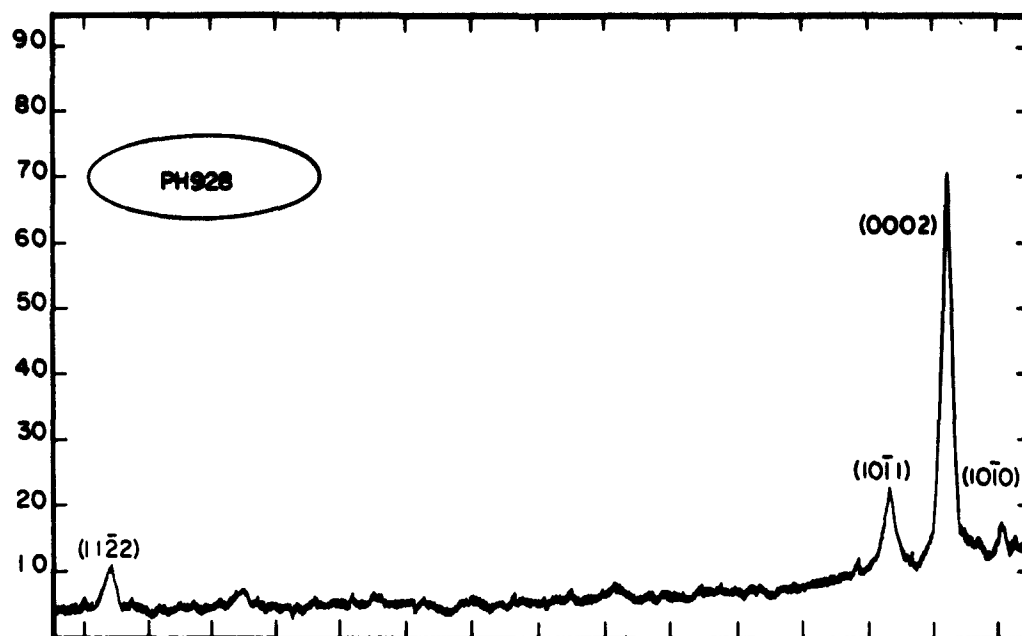


FIGURE 32 - CdS:Ag Film Sprayed at 200 ml/hr. Using Purified Chemicals; Sprayed on Pyrex Substrate at 315°C; Fair Luminescence.

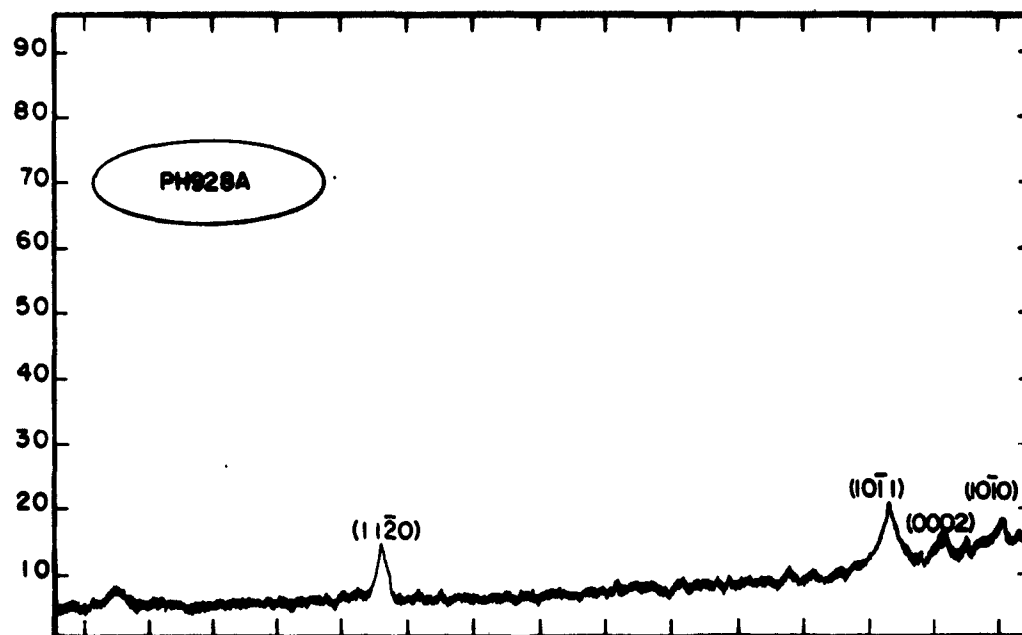


FIGURE 33 - Same as Above except Substrate Temperature 260°C; Poor Luminescence

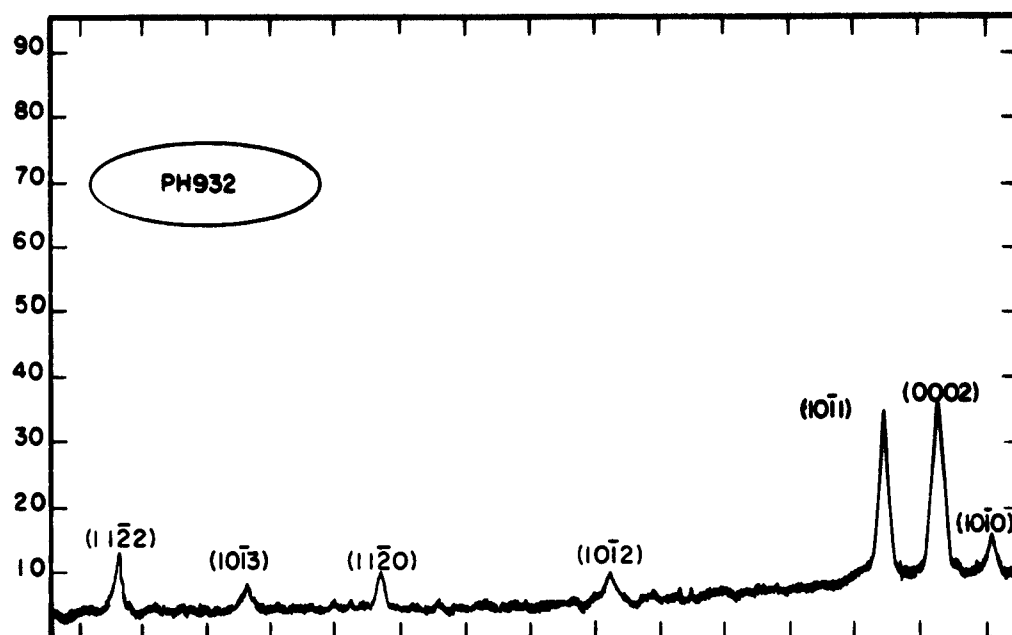


FIGURE 34 - CdS:Ag Film Sprayed at 200 ml/hr. Using Purified Chemicals; Sprayed on Soft Glass Substrate at 315° C; Good Luminescence.

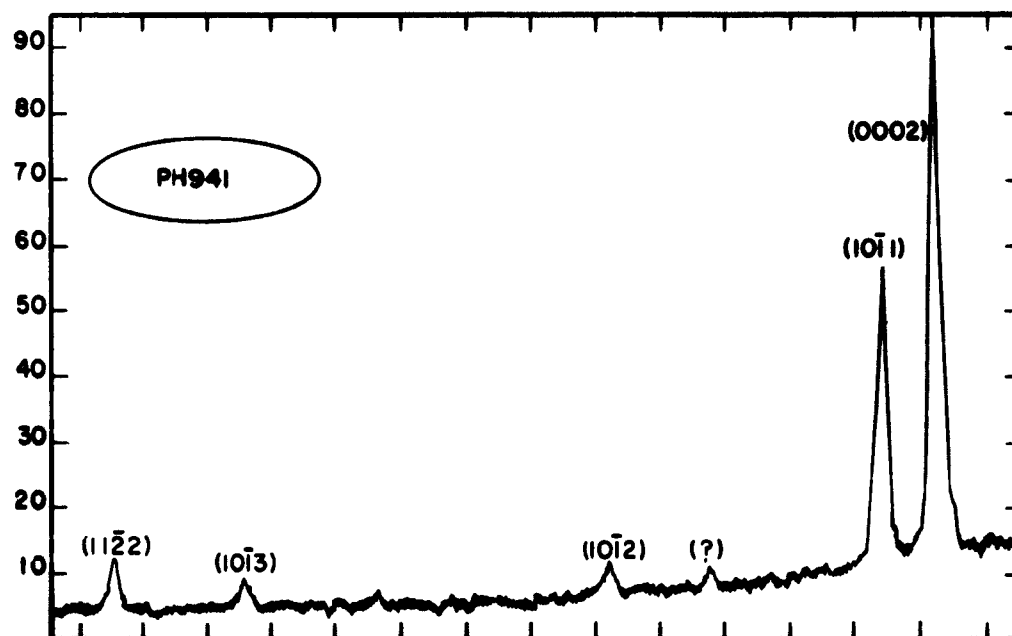


FIGURE 35 - Same as Above except Substrate of Pyrex; Good Luminescence.

TABLE 1
Trap Depths in the Silicate and Tungstate Films

Sample	Peak Glow Temperature °C	Trap Depth (ev)
$\text{Zn}_2\text{SiO}_4:\text{Mn}$	-140	0.27
	-108	0.33
	-22	0.50
	+15	0.58
	+150	0.87
ZnWO_4	-135	0.28
	-94	0.36
	-59	0.43
CdWO_4	-158	0.23
	-130	0.29
	-100	0.35
	-89	0.37
$\text{CdWO}_4:\text{Sm}$	-129	0.29
	-105	0.34
	-143	0.26
$\text{CdWO}_4:\text{Ce}$	-143	0.26
	-124	0.30
	-82	0.38

TABLE 2
Trap Distributions in the Sulfide Films

Sample	Thermoluminescence Temperature Range (°C)	Trap Depth Range (ev)	Glow Peak Temperature (°C)	Trap Depth (ev)
(3ZnS·CdS):Ag	-185 to -95	0.16 - 0.34	-159	0.23
(4ZnS·CdS):Ag	-180 to -90	0.18 - 0.36	-137	0.27
(5ZnS·CdS):Ag	-170 to -80	0.20 - 0.38	-120	0.31
(6ZnS·CdS):Ag	-170 to -70	0.20 - 0.40	-114	0.32
ZnS:Ag	-100 to -20	0.34 - 0.50	-62	0.42
	-170 to -80	0.20 - 0.38	-120	0.31

TABLE 3
Crystal Orientation in Cadmium Sulfide Films

Figure No.	Sample No.	Substrate	Solution Purity	Spray Rate	Spray Temp.	Heat Treatment	Luminescence	Orientation	Crystallinity
26	PH 915	soft glass	reagent, no silver	600 ml/hr.	260° C	none	poor	random	poor
27	PH 915 HT	"	"	"	"	650° C	fair	random	good
28	PH 911	soft glass	reagent, silver	600 ml/hr.	315° C	none	fair	(1120)	good
29	PH 911 HT	"	"	"	"	650° C	good	(1120)	good
30	PH 924	Pyrex	purified no silver	600 ml/hr.	260° C	none	very poor	random	poor
31	PH 924A	Corning 7056	"	"	315° C	none	very poor	(0002)	good
32	PH 928	Pyrex	purified, silver	200 ml/hr.	315° C	none	fair	(0002)	good
33	PH 928A	"	"	"	260° C	none	poor	random	very poor
34	PH 932	soft glass	purified, silver	200 ml/hr.	315° C	none	good	slight (0002)	good
35	PH 941	Pyrex	"	"	"	none	fair	strong (0002)	good

TABLE 4
Relative Intensities of X-ray Diffraction Peaks
for Randomly Oriented Hexagonal Cadmium Sulfide

Crystal Plane	Relative Intensities
(10 $\bar{1}$ 0)	78
(0002)	45
(10 $\bar{1}$ 1)	100
(10 $\bar{1}$ 2)	26
(11 $\bar{2}$ 0)	44
(10 $\bar{3}$ 0)	41
(20 $\bar{2}$ 0)	11
(11 $\bar{2}$ 2)	31
(20 $\bar{2}$ 1)	16
(0004)	6
(2022)	6
(10 $\bar{1}$ 4)	2

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